'DROP-IN' BIOFUELS:

The key role that co-processing will play in its production

Front cover information panel

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'DROP-IN' BIOFUELS: The key role that co-processing will play in its production

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THE POTENTIAL AND CHALLENGES OF 'DROP-IN' BIOFUELS - The key role that co-processing will play in production

SUMMARY

This update to the 2014 "drop-in" report was commissioned by IEA Bioenergy Task 39 with the goal of updating drop-in biofuels development, reviewing the status of technologies and the progress on the various technical approaches and assessing the challenges and obstacles that continue to restrict the large scale commercialization of drop-in biofuels. As described in the original report, "drop-in" biofuels are defined as "*liquid bio-hydrocarbons that are functionally equivalent to petroleum fuels and are fully compatible with existing petroleum infrastructure*".

As emphasised in the original report (2014), the oxygen present in biological feedstocks poses a significant challenge on the effective production of drop-in biofuels. Feedstocks with higher oxygen levels, such as sugars and most biomass, are more difficult to upgrade into drop-in biofuels as they require increased processing and greater volumes of hydrogen. The important role of hydrogen in upgrading biological feedstocks was emphasised as a key challenge for the future development of drop-in biofuels. This is even more pertinent now, particularly finding cheap and renewable sources of hydrogen. With stricter limits on sulfur in fuel standards worldwide and specifically in marine fuels (as set by the International Maritime Organisation[1]), global hydrogen demand will increase and place an additional burden on existing refinery capacity for hydrogen. The potential competition for hydrogen between petroleum refineries and drop-in biofuel refineries was highlighted in the 2014 report. However, as detailed in the current report, if a co-processing strategy with oil refinery integration is pursued, access to hydrogen should become a less significant obstacle to drop-in biofuel development. As well as co-processing strategies, the current report has assessed different hydrogen production technologies. Steam reforming of natural gas continues to be the most prevalent route to hydrogen production, as well as being the most cost-competitive under current conditions. It is anticipated that there will be increasing competition for hydrogen, both as

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potential fuel in its own right, but also within current and future refinery operations. For drop-in biofuels technologies where high hydrogen inputs are required, such as upgrading of pyrolysis/HTL bio-oils/biocrudes, the source of the hydrogen will have a significant impact on the life cycle assessment of these biofuels.

Petroleum refineries versus drop-in biorefineries

Drop-in biofuel production generally proceeds in two distinct phases that includes the production of an intermediate, e.g. pyrolysis oil, and a second phase of upgrading the intermediate into finished fuels. In the 2014 drop-in report, an in-depth summary of the refining of crude oil through different refinery processing steps was provided, including distillation, cracking and hydroprocessing. Many of these processing steps will also be needed to upgrade "biocrude/bio oil" intermediates into drop-in biofuels, although there are significant differences between crude oils and biological intermediate feedstocks. For all types drop-in biofuels some form of hydroprocessing is required (for every type of technology pathway) to make finished fuels, e.g. farnesene has to be converted into farnesane. For some biobased feedstocks, advanced processing such as catalytic cracking, isomerisation or fractionation is also required to allow the finished fuels to meet specifications. Currently, the dominant route to making drop-in biofuels has involved the upgrading of biobased feedstocks, primarily oleochemicals, in biorefineries. As detailed in the 2014 report this has been termed the oleochemical/lipid pathway with companies such as Neste, World Energy and others operating biorefineries that hydrotreat animal and vegetable fats/oils to produce biofuels. To date, this is the only pathway that has produced significant volumes of drop-in biofuels. However, to provide the much larger drop-in biofuel volumes that are needed it is likely that thermochemical technologies using biomass feedstocks will have to be commercialised. Unfortunately, progress to date has been slow, with the total volume of biocrudes/bio oils produced on a routine basis remaining low. Although some trials have occurred where biocrudes have been successfully upgraded to drop-in biofuels and this work has identified possible solutions to problems that have been encountered, they have tended more to highlight ongoing challenges. As will be detailed in the main body of the report, the initial stage of "advanced" (i.e. biomass derived) drop-in biofuel production, e.g. producing the intermediate, as demonstrated by companies such as BTG, Ensyn, etc., is often at a more advanced level of development than the second stage which involves the upgrading of the intermediate/biocrude into finished fuels. It is this second stage that most closely resembles petroleum refining and which offers enormous potential for cost saving through refinery integration. While refinery integration and/or co-

processing of biobased intermediates in existing refineries are prominently featured in this update, it is not the only route to upgrading biocrudes. As was covered extensively in the 2014 report, freestanding upgrading in biorefineries, as demonstrate by companies such as Neste, is also a viable approach.

The key role of refinery integration and co-processing

Although the potential for integration between petroleum refineries and biorefineries based on a co-processing strategy was briefly discussed in the 2014 report, in this update, co-processing is highlighted as being key to the expansion of drop-in biofuel production, specifically addressing the second, upgrading, stage. Utilisation of existing refinery infrastructure for co-processing of biobased intermediates will greatly facilitate the future development and expansion of low carbon drop-in biofuels by creating a commodity market for intermediates. This will enhance the accelerated production of liquid bio-based intermediates that can then be upgraded in bulk at existing refineries.

"Biocrude/bio oil" intermediates are quite distinct from crude oils as they will invariably have a higher oxygen content and a more reactive chemistry, which will undoubtedly impact refinery operations. Consequently, depending on the nature of the intermediate, various refinery processing units can potentially serve as suitable insertion points with the final selection of insertion points depend on the refinery configuration and the desired products. To date, most co-processing research has focused on hydrotreaters or fluid catalytic crackers (FCCs) as potential insertion points. As noted earlier, the FCC is the most flexible processing unit as it is able to tolerate a variety of feedstocks and no additional hydrogen inputs are required. The FCC cracks large molecules into smaller ones and is used primarily for gasoline production. "Cracking" of the large molecular weight intermediates that tend to predominate in many biocrudes/bio oils will be needed to produce drop-in biofuels. The FCC offers an "easier-and less-risky" insertion point in existing petroleum refineries. Another potential benefit is that the FCC catalyst is typically regenerated on site, which means that catalyst deactivation can be more readily addressed.

In contrast, hydrotreaters generally use expensive catalysts that are sensitive to inhibition and deactivation and which are typically regenerated off-site every few years. They are not usually used to crack large molecules into smaller molecules but rather as processing units to produce finished fuels (fuel blendstocks) by removing contaminants such as sulfur, nitrogen and oxygen (typically found at relatively low concentrations in fossil feeds).

The recent approval of ASTM 1655 that allows the co-processing of lipids at 5% blends in existing refineries should enhance the production of blended drop-in biofuels. Thus, it is likely that initial co-processing supply chains will be based on the "conventional/oleochemical" route where hydrotreaters or FCCs are used to co-process/upgrade lipid/oleochemical feedstocks. Lipids have a relatively lower oxygen content (11%), when compared to biomass, are chemically quite homogeneous, consequently making upgrading to drop-in biofuels significantly easier. In contrast, the biocrudes produced by pyrolysis and HTL routes generate more variable and complex bio-intermediate feedstocks that are more difficult to upgrade into finished fuels. The pyrolysis/HTL pathways are not currently certified by ASTM for the production of biojet fuels, using either freestanding upgrading or co-processing strategies and at this time, there does not appear to be an application under review. It is therefore likely to take longer to develop the supply chains for these intermediates within a co-processing strategy. Consequently, this can be seen as a more mid-to-longer-term strategy. As hydroprocessing will likely take longer to become established in the shorter-to-mid-term it is probable that biocrudes will be inserted into the FCC, based on the lower risk associated with this process.

Both conventional and advanced routes to drop-in biofuel production have been demonstrated, with the former already at a commercial scale. However, for both routes, ongoing research is still required to elucidate the behaviour of different biobased feedstocks in different reactors (chemistry and reactions) and the consequential impacts on the product characteristics. Equally important is the need to better determine the fate of the renewable carbon which will be distributed into the various product fractions, i.e., kerosene, gasoline, diesel, etc., produced during normal refinery operation. It is increasingly recognised that the renewable carbon content of the fuel will be a key metric when measuring the carbon reduction potential of finished fuels. This will likely form a central part of any policies designed to promote the production and use of drop-in biofuels. In parallel, techno-economic assessments of the different feedstock/reactor co-processing combinations will also be required to determine the economic viability of refinery integration.

It is likely that the various biobased intermediates, e.g. lipids, bio-oils and biocrudes, will originate or be produced from different feedstocks and various technologies, resulting in a range of chemical characteristics of these intermediates. Thus, to reduce the risk to the refinery, some form of "pretreatment/preliminary upgrading" of the biobased intermediates will be needed for stabilisation, removing contaminants, etc., prior to insertion into the refinery. If the "pretreatment/preliminary upgrading" step is situated at the refinery, a wider range of biobased intermediates could be accepted by

the refinery and allow faster commercialisation of co-processing. It is also likely that some sort of supportive policies and other incentives will be required to encourage refineries to assess these types of co-processing strategies.

Progress in drop-in biofuel commercialisation - oleochemical pathway

Of the various drop-in biofuels that are currently being produced, renewable diesel is, by far, the largest volume product, with the vast majority of the renewable diesel derived from the hydrotreating of oleochemical feedstocks of lipids/oleochemicals. It is also very likely that renewable diesel will remain the most significant source of drop-in fuels in the near term. The production of oleochemical derived, "conventional" drop-in biofuels will help establish much of the supply chain that will be needed for "advanced" drop-in biofuels based on biomass feedstocks that are anticipated to be more plentiful and cheaper. The oleochemical route is also the major supplier of biojet fuels, with dedicated biojet fuel production taking place at World Energy (formerly Alt Air) in California. However, even in this facility, renewable diesel remains the major product. Current global, renewable diesel production is about 5 billion litres annually, dominated by freestanding facilities based on hydrotreating. More recently there has been a trend towards conversion of existing, disused refinery infrastructure into renewable diesel refineries. Examples include ENI (Italy), Total La Mede (France) and the announcement by Andeavour to convert a refinery in North Dakota[2].

As was highlighted in the 2014 report the two main challenges of the oleochemical pathway are the feedstock cost/availability and the overall sustainability of the feedstock. As an example, some oleochemical feedstocks such as vegetable oils often cost more per tonne than the finished fuels. The competition between food and fuel has also been an ongoing concern, driving policy in jurisdictions like the EU. However, policies to support climate mitigation in other jurisdictions have played a big role in driving the ongoing production of oleochemical drop-in biofuels, to some extent overcoming the price differential. Jurisdictions such as California and British Columbia have been a major destination for renewable diesel based on the low carbon fuel standards in place. The producer incentive for biobased diesels in the USA have also boosted the production of diesels, rather than jet fuels.

To try to resolve the feedstock cost and sustainability challenges associated with the oleochemical/conventional drop-in biofuels route, various companies have adopted two approaches.

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[2] http://www.andeavor.com/refining/dickinson/dickinson-refinery-renewable-diesel-upgrade-project/

The predominant strategy has been to use "wastes" such as used cooking oil, tallow and even brown grease. However, these feedstocks are in limited supply and this has led to increased trade in used cooking oil, tallow and fish fats and oils with countries such as China, New Zealand and Australia exporting to "upgrading" facilities in Rotterdam and Singapore. The second approach that has been pursued is the development of alternative, "lipid" feedstocks such as jatropha, camelina, carinata, etc., with the supposition that these crops will be grown on marginal lands, minimising land use concerns. Although these approaches are ongoing, the development of new feedstock supply chains (from farmer to processing) have proven challenging and, at this time, only limited volumes of alternative feedstocks are available.

Progress in drop-in biofuel commercialisation - thermochemical pathways

The 2014 report suggested that thermochemical technologies, based on more widely available and supposedly cheaper feedstocks such as biomass residues, will provide the long-term supply of drop-in biofuels. However, commercialisation of these technologies has proven challenging with the lack of long-term policy support also hampering development. As summarised below, the two predominant thermochemical routes to producing drop-in biofuels are via gasification and pyrolysis/hydrothermal liquefaction.

For many decades, drop-in, commercial, finished fuels have been made using gasification combined with Fischer-Tropsch synthesis with coal and natural gas used as the feedstocks. In 2008 this pathway to making alternative jet fuel was the first to receive ASTM D7566 certification with the South African company Sasol championing this application, based on coal as the feedstock. However, when various group have tried to develop variations of this technology using biomass as the feedstock, significant challenges have been encountered. These included high initial investment costs, syngas cleanup after biomass gasification proving possible but expensive, biomass was not such a low cost feedstock as was anticipated, and the scale of facilities based on coal and natural gas proved difficult to reproduce using biomass feedstocks.

To try to resolve some of these challenges more recent gasification platforms, such as plasma gasifiers, have been shown to produce very clean syngas, overcoming the significant challenges of syngas cleanup. However, plasma gasifiers have proven expensive to build and operate with projects such as Solena's facility in the United Kingdom currently on hold. Other groups such as Fulcrum Bioenergy, who initially looked at plasma gasification, switched to a bubbling fluidized bed technology, even though these gasifiers

generally produce higher tar levels. Fulcrum has tried to resolve this issue by combining this technology with steam reforming technology to produce cleaner syngas. Currently the Fulcrum Bioenergy facility is under construction in Nevada and completion is expected by 2020[3]. Although the company is targeting aviation or biojet fuels, this will only be a portion of the FT derived hydrocarbon mixture of liquids and fractionation and upgrading steps will still be required to make any drop-in biofuels. Other companies that are pursuing the gasification of biomass route to drop-in biofuels include Velocys, who are developing small-scale Fischer-Tropsch technology at their ENVIA Energy plant based on gas-to-liquids conversion[4]. Red Rock Biofuels is following a related approach, using gasification of wood combined with FT synthesis (provided by Velocys) to build their demonstration plant[5].

The other major thermochemical route to drop-in biofuels involves the initial production of liquid intermediates via pyrolysis or hydrothermal liquefaction (HTL), followed by subsequent upgrading. While fast pyrolysis has been commercialised by companies such as Ensyn and BTG, the upgrading step of converting bio-oils to finished fuels has not yet been commercialised. Although hydrothermal liquefaction (HTL) based companies such as Licella and Steeper can produce a lower oxygen, likely more stable, biocrude, this route to intermediates is still at the pilot/small demo scale. However, both companies are actively pursuing commercialisation with a focus on the engineering challenges of scaling up a high pressure reactor. Although an advantage of using HTL is that it is able to use wet feedstocks one of the previously identified challenges to bio oil/biocrude upgrading includes the still, quite high, oxygen content of these intermediates. This poses significant challenges for upgrading and a requirement for high volumes of, ideally, renewable hydrogen for upgrading. The development and use of cost-effective and longer lifespan catalysts is another ongoing challenge with various pretreatment strategies used to try to filter and remove potential contaminants such as alkali metals (which contribute to polymerisation). Another alternative approach is catalytic pyrolysis that can produce liquid intermediates with a lower oxygen content, greater stability and which are easier to upgrade into finished fuels. However, it appears that current catalytic pyrolysis work is at an earlier stage of development and experiencing lower yields per kg of feedstock, rapid catalyst deactivation and challenging economics.

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[3] https://www.prnewswire.com/news-releases/fulcrum-bioenergy-breaks-ground-on-sierra-biofuels-plant-300649908.html
[4] https://www.velocys.com/envia-oct-2017/
[5] https://www.biofuelsdigest.com/bdigest/2018/07/29/red-rock-biofuels-facility-breaks-ground-in-lakeview/

Although a more stable bio-oil or biocrude with lower oxygen is highly desirable and easier to upgrade, the same type of upgrading infrastructure will still be required to crack and hydroprocess the liquid intermediate into the strictly specified finished fuels[6]. An ongoing consideration has been the trade-off between the production of a low-oxygen intermediate (such as an HTL derived biocrude) which will require less upgrading, as compared to a high-oxygen content intermediate (such as a pyrolysis derived biocrude) which will require more upgrading. It should be noted that upgrading of any of the liquid intermediates derived from any of the thermochemical liquefaction technologies via refinery integration and co-processing is, potentially, a viable solution for all cases. However, significantly more research is still needed so we can better understand the behaviour of the various biobased-intermediates during co-processing and the economic potential of the various strategies.

Progress in drop-in biofuel commercialisation - biochemical and hybrid pathways

It was previously suggested that the various biochemical routes to drop-in biofuels were unlikely to be economically attractive primarily because, in the vast majority of cases, the biochemical intermediates would be worth more than the finished fuels. For example, most biochemical pathways produce highly functionalised molecules that make them more suitable for applications in the broader biochemical sector. However, companies such as Amyris, Gevo and Lanzatech continue to actively pursue drop-in biofuel production with these companies placing a focus on biojet fuels. This route to biojet fuels has received ASTM certification, giving these fuels ready market access and a significant demand for the limited supply. As a result, a good number of flights using either the direct sugar to hydrocarbon pathway (DSHC) or the alcohol-to-jet (ATJ) pathways (isobutanol to jet and ethanol to jet) have occurred and have received considerable publicity. However, it is likely that the cost competitiveness of biojet derived via this route will continue to be challenging.

Over the last few years there has been increased interest in the Power-to-Liquid (PtL) fuels route to drop-in fuels production, particularly in Europe. This technology is based on carbon capture technologies combined with renewable hydrogen generation through electrolysis of water and the synthesis of longer chain hydrocarbons through technologies such as Fischer-Tropsch. If successful, this pathway offers significant advantages as these drop-in fuels can be used within existing infrastructure while avoiding the sustainability challenges that are sometimes associated with biomass use. The Power-to-Liquid (PtL) fuels

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[6] Low specification fuels such as heating oil or heavy fuel oil (for shipping) may require less upgrading

route can also serve as a form of "energy storage" by using excess renewable electricity to create liquid hydrocarbon fuels. However, it is anticipated that the considerable economic challenges will limit the development of the Power-to-Liquid (PtL) fuels route.

The role of policy in development of drop-in biofuels
As indicated earlier, long term, supportive policies that ensure stability to both producers and users of drop-in biofuels will be key to ensuring the full commercialisation of drop-in biofuels. However, volumetric mandates alone will not be adequate if climate change mitigation is a primary goal as the low carbon intensity (CI) of the drop-in biofuel will have to be ensured. As one example, the low carbon fuel standards that have been legislated in jurisdictions such as California and British Columbia have played a key role in drop-in biofuel production. These types of policies, which rewards those biofuels that have the greatest emission reduction potential, must become more widespread if drop-in biofuel production and use is to become more widespread. In addition, sectors such as aviation, which is uniquely reliant on the development of lower carbon intensity drop-in biofuels, will likely require specific policies to support the production and consumption of so-called sustainable aviation fuel (SAF)/biojet fuel.

It is likely there will be increase levels of electrification for transport in urban areas, with related factors such as air pollution, congestion, shared-economy, etc., all contribution to the development of electric cars. However, sectors such as aviation, marine, rail and long distance trucking are predisposed to wanting access to low carbon intensity, drop-in biofuels. As mentioned earlier, the current oleochemical and the future biocrude routes to drop-in biofuels results in the production of multiple products including biodiesel, biogasoline and biojet fuel fractions. As drop-in biofuels are fully compatible with the existing fossil-fuel transportation infrastructure they can be used in high blends or even neat (depending on fuel standards) to achieve significant emission reductions. It is likely that the initial drop-in biofuels supply chain will be developed using lipid feedstocks and the oleochemical/conventional route to drop-in production. The challenge is not the technology, but the cost, sustainability and availability of the lipid/oleochemical feedstock. In the mid-to-longer term, thermochemical pathways that make use of lower-cost, greater volume lignocellulosic feedstocks will have to be used to supply the significant volumes of drop-in biofuels that will be needed by the long distance transport sectors. As high blends or "neat" drop-in biofuels are fully compatible with the current petrochemical infrastructure there is considerable potential to achieve significant emission reductions. Currently, transportation accounts for

23% of the global energy related CO_2 emissions and this is expected to increase as the economies of countries such as India and China continue to expand. As biofuels, primarily ethanol and biodiesel, only represent about 4% of worlds current transportation fuel supply, there is significant room for expansion of drop-in biofuel production and use, with the expectation that this will contribute significantly to the world meeting its climate mitigation targets.

General conclusions

The only significant volumes of drop-in biofuels that are currently produced are renewable diesel based on the oleochemical pathway which involves the upgrading of lipids via hydrotreatment. In the short-to-medium-term, this pathway will continue to supply the majority of drop-in biofuels, particularly for renewable diesel and biojet fuel (Sustainable Aviation Fuel/SAF) markets. The production and use of these so-called "conventional" drop-in biofuels will help establish the supply chains, policy and sustainability/carbon intensity (CI) criteria that will be needed to facilitate the development of "advanced" drop-in biofuels derived via thermochemical based processes using biomass as the feedstock.

As well as developing policies that encourage the production and sustainability of the feedstocks/intermediates (e.g. lipids/biocrudes) that will be needed, the second, "upgrading" step of drop-in biofuel production will also need policy support. Although the need for better integration of petroleum refineries and drop-in biofuel production was discussed previously, in this update, co-processing, specifically the second, upgrading, stage is highlighted as being key to the future expansion of drop-in biofuels. Utilisation of existing refinery infrastructure for co-processing of biobased intermediates will greatly facilitate the future development and expansion of low carbon drop-in biofuels by creating a commodity market for intermediates. This will enhance the accelerated production of liquid bio-based intermediates that can then be upgraded in bulk at existing refineries.

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Foreword

Much of the background material that was detailed in the original, 2014, IEA Bioenergy Task 39 "The Potential and Challenges of Drop-in Biofuels" report is still very relevant and has been either summarised, reproduced or slightly re-written in the current, updated report. In the intervening years good progress has been made in several of the technologies, some new projects have been announced, with some moving towards demonstration/commercial scale. Although some technologies are currently stalled or on-the-back-burner, the basic categories and operating theories of drop-in technologies have remained largely the same.

Although the aviation sector continues to play a leadership role in championing the development of drop-in biofuels the imminent global requirement to reduce sulphur emissions from the marine sector encouraged IEA Bioenergy Task 39 to commission a specific report on Biofuels in Marine Shipping. This report can be accessed and downloaded from the [Task 39 website](). We hope to soon release a similar, updated report on Biofuels in Aviation in the near future.

As is covered in much more detail in this current report, oil refinery integration will be key to the future development of significant volumes of drop-in biofuels. Although the need for better integration of petroleum refineries and drop-in biofuel production was discussed previously, in this update, co-processing, specifically the second, upgrading, stage is highlighted as being key to the future expansion of drop-in biofuels. It is suggested that better utilisation of existing refinery infrastructure for co-processing of biobased intermediates will greatly facilitate the future development and expansion of low carbon drop-in biofuels by creating a commodity market for intermediates produced via either the oleochemical based "conventional", or the biocrude/bio-oil based "advanced" drop-in biofuel routes. This will enhance the accelerated production of liquid bio-based intermediates that can then be upgraded in bulk at existing refineries.

This current report also synergises with other Task 39 work as well as with the work of other IEA Bioenergy Tasks and related work carried out by other IEA TCP's and organisations such as IRENA, GBEP, etc. IEA Bioenergy Task 39 recently published (www.Task39.org) an "Implementation Agendas" report, that compares-and-contrasts the various policies that member countries have used to encourage the production and use of biofuels. We also publish a database on demonstration level biofuel facilities that is updated annually and can be accessed at http://demoplants.bioenergy2020.eu/.

While Task 39 is focused on production of liquid biofuels, the IEA Bioenergy Tasks on Gasification (Task 33) and Direct Thermochemical Liquefaction (Task 34) address the underlying technologies in greater depth, without limiting themselves to liquid biofuels for transportation.

Gasification Task - http://www.ieabioenergy.com/task/thermal-gasification-of-biomass/

Direct Thermochemical Liquefaction task - http://www.ieabioenergy.com/task/pyrolysis-of-biomass/

The future work of IEA Bioenergy over the next triennium will feature an integrated project between these different Task groups.

In the intervening four years since the last "The Potential and Challenges of Drop-in Biofuels" report was published, what has become apparent is that technology/commercialisation cannot function in isolation, particularly during times of relatively low oil prices and when transport related carbon emissions are not costed. Without long-term supporting policies, companies will struggle to fully commercialise drop-in biofuels technologies as it is likely that, for some time, drop-in biofuels will be more expensive than fossil-based transportation fuels. Thus, the development of significant volumes of drop-in biofuels will require significant, long-term and stable policy support. As well as policies, achieving a consensus on how the overall carbon intensity of a drop-in biofuel is calculated is still needed. Currently Task 39 has an ongoing project that is comparing-and-contrasting several of the main life cycle assessment (LCA) models that are used to calculate the sustainability and GHG intensity of various biofuels. This report will be released in 2019 and will form the basis of future work where, as well as assessing the commercial readiness of the various routes to drop-in biofuels production, the carbon intensity of the various processes and products will also be assessed.

1. INTRODUCTION

Biofuels are renewable alternatives to fossil derived transportation fuels with the ability to achieve environmental and socioeconomic benefits such as reduced GHG emissions, employment generation and energy security. Bioethanol and biodiesel are the main commercially available biofuels. In 2017 140 billion litres of these fuels were produced which was just over 4% of global transportation energy demand[7]. However, these fuels are chemically and functionally different from petroleum-derived fuels and thus cannot make full use of the existing petroleum processing and distribution infrastructure. As infrastructure components, such as vehicle engines, fueling stations, refineries, etc., are very expensive to change, it is generally recognised that biofuel use would be greatly enhanced if biofuels were "functionally equivalent to current petroleum-derived fuels and could be readily "dropped-into" the existing infrastructure (petroleum distribution and refining, fuel specifications, etc.). Thus, as defined in the first edition of this report:

"*Drop-in biofuels are liquid bio-hydrocarbons that are functionally equivalent to petroleum fuels and are fully compatible with existing petroleum infrastructure"*.

In this update of the report the technology pathways by which "drop-in" biofuels can be produced, continue to be summarised in the four broad categories below:

- Oleochemical,
- Thermochemical,
- Biochemical, and
- Hybrid pathways.

Subsequent chapters examine the basic principles of the technology pathways and many of the companies that are involved drop-in biofuel development. This is not intended to be a comprehensive list of companies, but a technology overview highlighting some of the key players. As we have tried to make this report a relatively concise update of the original 2014, repetition has been minimised and the reader is encouraged to read the 2014 report as much of this inflation is still very relevant today.

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[7] https://www.iea.org/tcep/transport/biofuels/

As detailed in the original report producing "drop-in" biofuels will require much more complex processing infrastructure and higher processing inputs than today's predominant bioethanol and biodiesel biofuels. This leads to greater techno-economic challenges when trying to develop cost competitive routes to drop-in biofuels as many drop-in biofuels production processes show large similarities, and potential synergies, with the production of transportation fuels from crude oil.

As described previously and discussed below, lipid and biomass feedstocks contain high levels of molecular oxygen which must be removed to produce drop-in bio-hydrocarbon fuels (See section 1.2). This highlights the increasing need for, ideally "green", hydrogen as drop-in biofuel production expands. Hydrogen is currently a key input for the oil and gas sectors where it is used to upgrade crude oil to refined products. The increased use of lower quality crudes that have higher sulfur content and longer hydrocarbon chains, has led to increased demand for hydrogen in the refining sector. In addition, stricter sulfur limits in sectors such as shipping will put increasing pressure on refineries to produce higher quality fuels, requiring higher volumes of hydrogen for upgrading. As biofuel production increases and the need for hydrogen increases, drop-in biofuel producers will have to compete with both the petroleum sector as well as the ammonia fertilizer industry for this resource. Hydrogen requirements and sourcing is a central theme throughout the update of the report with the "hydrogen dilemma" and its impact on production and techno-economics of drop-in biofuel production discussed in detail[8].

Global climate reduction goals will require extensive decarbonisation of transport (as indicated in the quote from IEA below), particularly in sectors where electrification is not a suitable option (such as long-distance trucking, shipping and aviation).

"In 2015, the transport sector accounted for 23% of global energy-related carbon dioxide (CO_2) emissions and remains the least diversified end-use sector with 93% dependence on oil (IEA, 2016c). Therefore, limiting global temperature rise to well below 2°C as per the United Nations 21st Conference of the Parties (COP21) global climate agreement will require significant decarbonisation of the sector. Biofuels make a key contribution within the International Energy Agency (IEA) long-term 2 Degree Scenario (2DS),

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[8] This issue was highlighted in an article in Biofuels Digest based on the first publication of this report. https://www.biofuelsdigest.com/bdigest/2014/08/11/the-hydrogen-wall-looking-at-the-prospects-for-drop-in-biofuels/

especially within non-urban transport where opportunities for electrification are more challenging" (IEA 2016).

Regardless of the unfavourable economics for biofuels in a low oil price environment, biofuels will play an essential role in decarbonisation of transport. Thus, policies that support their development will be crucial. Biofuel mandates have offered some protection against low oil prices (IEA 2016). However, mandates have generally been restricted to conventional biofuels and been limited in their promotion of advanced (and drop-in) biofuels. While conventional biofuels will continue to play an important role in decarbonisation of transport, biofuels that target long-distance transport will need aggressive development in the future. This will also need a shift in the type of policies used, as policies such as volumetric mandates do not take carbon intensity into account. Thus, reshaping the policy framework around the carbon intensity of biofuels must become more important if real emission reductions are to be achieved.

Policy has been instrumental in promoting biofuels production and consumption and will continue to play a key role in the future, particularly during periods of low oil prices. Past and current biofuels policies have been primarily volumetric and do not have any specific sustainability requirements. However, as climate change mitigation will be a major driver for future biofuels development, the carbon intensity of biofuels will become an increasingly important metric. The overall sustainability and carbon intensity of a biofuel is typically assessed via life cycle assessment (LCA) with various countries and regions using different models such as GREET (US), BioGrace (EU), GHGenius (Canada) and the Virtual Sugarcane Biorefinery (VSB) in Brazil. In a separate, soon to be published report, IEA Bioenergy Task 39 has been comparting-and-contrasting the various LCA models and the various assumptions within the models that have resulted in some differences in the carbon intensity values that have been reported.

As mentioned earlier, the aviation sector has been a long term champion for the development of drop-in biofuels and sustainable aviation fuels (SAF)/biojet fuels in particular. However, biojet fuels are high specification fuels, are more costly to produce and jet fuel (Kerosene) does not earn a premium against other fuels such as diesel. To add to the challenge, the sector has no real alternative ways to decarbonise as new technologies for propulsion are still decades away while the life expectancy of aeroplanes is several decades at least. Aviation is also a difficult sector in which to develop a policy strategy as aeroplanes typically operate across many national borders where different regulations apply. As one example, international aviation is excluded from the COP21 agreement on reduction of emissions and the industry

is currently expected to self-regulate through the International Civil Aviation Organisation (ICAO). Although the recently agreed Carbon Offset and Reduction Scheme for International Aviation (CORSIA)[9] allows airlines to purchase offsets to reduce the impact of emissions, there is no requirement for them to purchase and use low carbon fuels.

As discussed earlier and detailed below, if drop-in biofuels are to be produced in the volumes that will be needed by the aviation sector a co-processing strategy will have to be adopted, with oil refineries playing a key role and lower carbon gasolines, diesel, etc., factions also produced as well as the biojet fraction. Thus, a major focus of the current update is to describe how the nature of the feedstock/intermediate will influence the most likely insertion point when lipids/biocrudes are upgraded in a refinery and the range of lower carbon drop-in biofuels that will likely be produced.

1.1 DROP-IN BIOFUELS – DEFINITION AND PROPERTIES

Conventional biofuels such as bioethanol and biodiesel (fatty acid methyl esters -FAME) have distinct chemical functional groups and can be accurately described based on their chemical composition alone. In contrast, drop-in biofuels generally consist of a mixture of many different types of hydrocarbons, the properties of which, just like petroleum fuels, are typically characterized by the functional characteristics of the mixture, such as distillation profile, viscosity, acidity, etc.

As noted earlier, conventional biofuels such as bioethanol and biodiesel have various limitations:

- Conventional biofuels are chemically and functionally different from petroleum-derived fuels and thus cannot make full use of the existing petroleum processing and distribution infrastructure. Unless modified engines are used, these biofuels can only be used in relatively low blends (ethanol maximum 15% and biodiesel 20%)[10].
- Conventional biofuels are unsuitable for use in sectors such as aviation and long distance trucking as they do not meet the density requirements or other specifications of such fuels.
- Currently, conventional biofuels predominantly use "food-based" feedstocks such as corn, sugarcane and vegetable oils. Food security concerns and questions of sustainability will continue to encourage the production of biofuels from wastes or lignocellulosic materials that is more abundant and not in competition with food. This requires different types of technologies.

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[9] https://www.icao.int/environmental-protection/CORSIA/Pages/default.aspx
[10] https://www.afdc.energy.gov/fuels/biodiesel_blends.html

- The extent to which conventional biofuels can reduce emissions (carbon intensity) is generally also lower than biofuels made from lignocellulosic feedstocks (although this is not always the case).

While drop-in biofuels are sometimes described as oxygen-free, it should be noted that crude oil itself can sometimes contain up to 2 wt% oxygen (infrequently, even more) (Speight, 2006). It should also be noted that blend limits may sometimes be applied to drop-in biofuels. For example, renewable jet fuels that have been derived via hydrotreatment typically do not contain aromatics which are important in airplane fuel systems to maintain seal integrity. Therefore, blends of up to 50% are permitted by ASTM D7566 in order to meet overall fuel specification[11]. Similarly, other drop-in biofuels (on their own) may not comply with all of the specifications within a certain fuel standard and, as a result, may have to be used in prescribed blends.

Within this report the term blendstock is used to describe the mixture of hydrocarbons that can be fractionated into gasoline (petrol), diesel, jet and other types of commercial transportation fuels, whether lipid/biomass or petroleum derived. Blendstocks are typically defined as refinery precursors that are processed in existing refineries, pipelines or anywhere upstream of a blending terminal in the petroleum supply chain. It is important to note that, apart from some biochemical pathways to drop-in biofuel production, most of the drop-in biofuel technologies produce a blendstock as a product, which requires further separation through processes such as distillation.

It is also apparent that drop-in biofuels are better positioned than bioethanol or biodiesel to avoid blend wall concerns (although blend limits may still apply)[12] and can potentially make better use of existing infrastructure (current inventory of petroleum refineries, supply channels and liquid fuel powered combustion engines). With the exception of flex-fuel vehicles (FFVs) and E85 vehicles, most jurisdictions outside of Brazil blend ethanol at levels that do not exceed 10% by volume (E10)[13].

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[11] https://www.astm.org/Standards/D7566.htm

[12] For example, farnesane is limited to blends of 10% in aviation fuel and paraffinic drop-in biofuels such as HEFA are limited to 50% blends in aviation fuel. Recently, ASTM certification was also achieved for alcohol-to-jet fuels based on isobutanol and blends are limited to 30%. Most of these limits are applicable to aviation as biojet fuels are paraffinic in nature while aviation fuel requires a minimum aromatic content to ensure seal integrity.

[13] Although this is to some extent due to constraints of the internal combustion engine, it is also a political issue with the fossil sector protecting their market. Apart from older vehicles, ethanol can easily be used in up to 15% blends with no adverse consequences.

1.2 DEOXYGENATION OF BIOMASS

The greatest challenge that is and will continue to be encountered during the conversion of biomass into drop-in biofuels is the removal of the oxygen present in biomass in the form of the various chemical functional groups such as esters, ethers and hydroxyl groups. While oxygen is potentially valuable for metabolic processes and in some value-added chemicals, it is highly undesirable in drop-in biofuels. As shown in Figure 1, biodiesel and bioethanol are only partially deoxygenated and this is one of the main reasons why these conventional biofuels are not fully compatible with the existing petroleum infrastructure. These oxygenated functional groups are hydrophilic and can react with refinery and pipeline metallurgy as well as with biofuel components to form gums, acids and other impurities, to the detriment of biofuel storability/stability (Pearlson, 2011; Bridgwater, 2012).
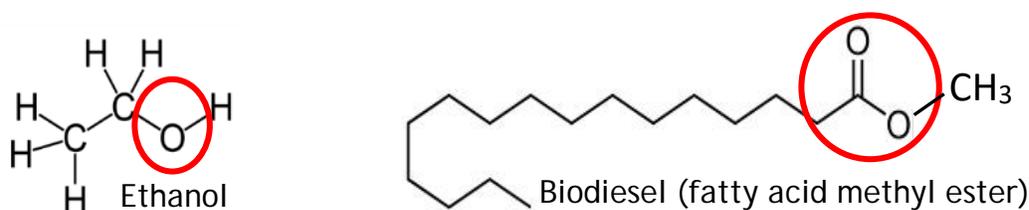
Figure 1 Current commercial biofuels and their oxygen content

Compatibility and reactivity are not the only reasons why it is important to deoxygenate biofuels as the oxygen in biofuels also reduces their energy density. This in turn determines the size of a vehicle's fuel tank which, consequentially, determines travel range for all modes of transportation. As indicated below, the energy density of biofuels and biomass processing intermediates decreases linearly (Figure 2) with increasing oxygen content (expressed as the molar ratio of oxygen to carbon (O/C) in the fuel molecule).
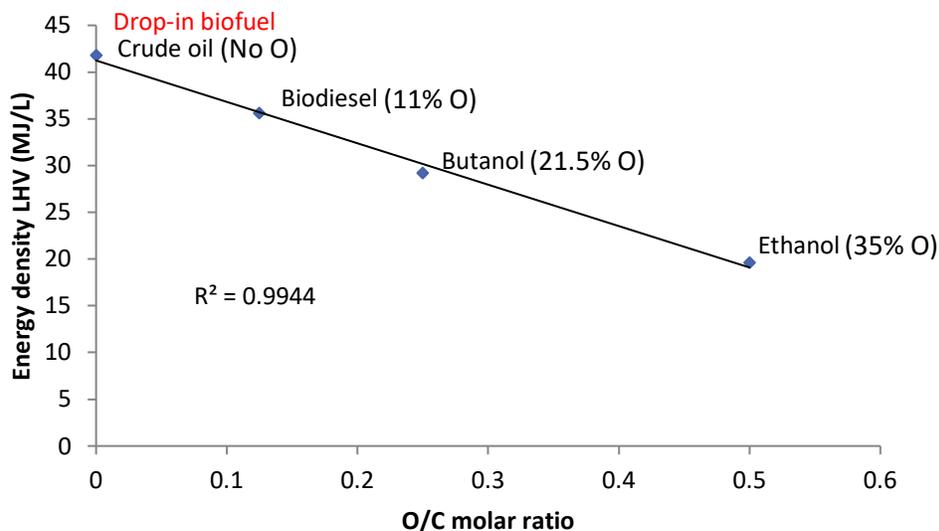
Figure 2 The influence of oxygen content on the energy density of liquid fuels

1.2.1 The Hydrogen-Biomass feedstock dilemma (or trade-off)

As summarised earlier, the deoxygenation of biomass intermediates is achieved through three main chemical reduction processes: (1) hydrodeoxygenation (HDO) (producing H_2O), (2) decarboxylation (DCO) (producing CO_2) and (3) decarbonylation (producing CO & H_2O). These reactions are illustrated below using the deoxygenation of fatty acids as an example (Figure 3), but are generally applicable to the deoxygenation of any oxygen-containing feedstock.
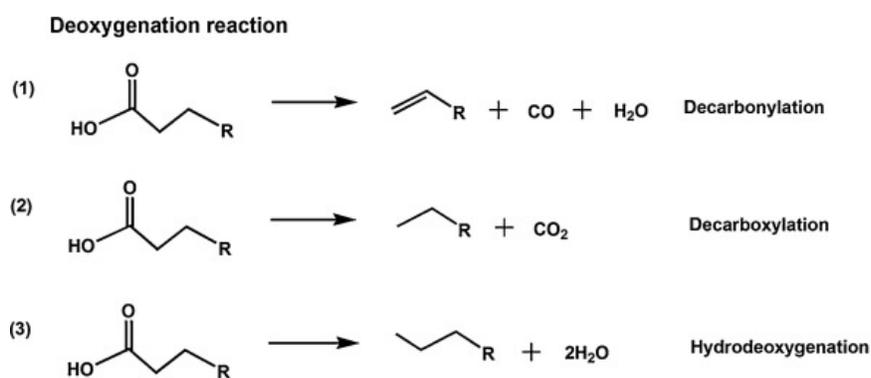
Figure 3 Deoxygenation reactions (Gosselink et al. 2013)

During hydrodeoxygenation the hydrogen present in the biomass intermediates (or supplied externally) is oxidized with the oxygen subsequently removed as water (H_2O). During decarboxylation the carboxyl group carbon is oxidized and the oxygen is removed as carbon dioxide. During decarbonylation, oxygen is removed as carbon monoxide with a water molecule also formed. While reaction conditions can be adjusted to favour one reaction (e.g. the type of catalyst used), in practice these processes take place simultaneously. The HDO process is typically favoured when hydrogen is externally added (e.g. hydrogen gas derived from natural gas) while, in the absence of hydrogen, the DCO route is favoured (NSF 2011; Pearlson 2011). However, it is interesting to note that some co-processing studies that used a fluid catalytic cracker (where no additional hydrogen is added), resulted in hydrogen transfer between molecules with all three reactions taking place (from fossil molecules to biomolecules) (Pinho et al. 2015, 2017).

When decarboxylation or decarbonylation takes place, the carbon in the feedstock is lost by oxidation and, as a result, the yield of hydrocarbons is reduced. When hydrogen inputs are used to remove oxygen, yields of hydrocarbons are generally higher, but the cost and sustainability of the imported hydrogen has to be considered. Although deoxygenation can be achieved either biologically or thermochemically, the trade-off between hydrogen inputs and process yields remains unchanged. In all cases, the ultimate objective is to, not only to deoxygenate biomass intermediates, but to also enrich the carbon chains in hydrogen, thus elevating their low H/C ratio to the level of finished petroleum transportation fuels (H/C of about 2).

During deoxygenation, some of the products formed are gaseous (typically CO and CO_2). In most cases they should be removed or they will likely cause numerous problems such as altering the hydrogen partial pressure, inhibiting catalyst activity and the formation of carbonic acid in the effluent, resulting in corrosion. At elevated temperatures, the CO can react with hydrogen to form methane, diverting hydrogen away from the final fuel and increasing hydrogen consumption. While CO_2 is easier to remove (through amine scrubbers), CO is far more difficult to remove from gaseous products.

1.2.2 The Hydrogen to Carbon ratio

The hydrogen to carbon ratio (H/C ratio) is a convenient metric used by the petroleum and coal sectors to indicate how hydrogen-rich and energy dense various fossil feedstocks are. During the production of

drop-in biofuels one of the main objectives is to elevate the low H/C ratio of the biomass feedstock to that of diesel, jet and gasoline fuels which have H/C ratios closer to 2.

During combustion, the oxygen within the biomass consumes hydrogen and thus reduces the effective H/C ratio. Thus, using a biomass feedstock where the main elemental components are hydrogen, carbon and oxygen, the H/C ratio must account for the relatively high level of oxygen (in contrast to petroleum feedstocks which contain practically no oxygen), as each oxygen atom consumes two hydrogen atoms to form a water molecule (H_2O) that contributes no energy to the combustion system (Vennestrøm et al. 2011). Thus, the "effective" H/C ratio for oxygenated biomass feedstocks, H_{eff}/C, is calculated by Equation 1.

$$H_{eff}/C = \frac{n(H) - 2n(O)}{n(C)}$$ where n=number of atoms of each element

(The Effective Hydrogen to Carbon ratio)

Highly oxygenated and hydrogen-poor biomass intermediates such as sugars and cellulosic biomass have low H_{eff}/C ratios with glucose having an H_{eff}/C ratio of zero. The H_{eff}/C ratios of some common biofuel intermediates, as well as drop-in diesel molecules, are depicted along a "staircase" in Figure 4 with the stairs signifying hydrogen inputs required to produce the final fuel. The bigger the gap between the H/C ratio of a feedstock and the ratio of a target product molecule, the more processing and hydrogen inputs ("steps") are required. A lipid feedstock, for example, has a H/C ratio of 1.8 and requires fewer hydrogen inputs to reach a target H/C ratio of 2. Therefore drop-in biofuel production through the oleochemical platform has fewer inputs and "steps" to take compared with a lignocellulosic biomass feedstock for drop-in biofuel production starting from an H/C ratio of 0.2 (Forsberg 2009).
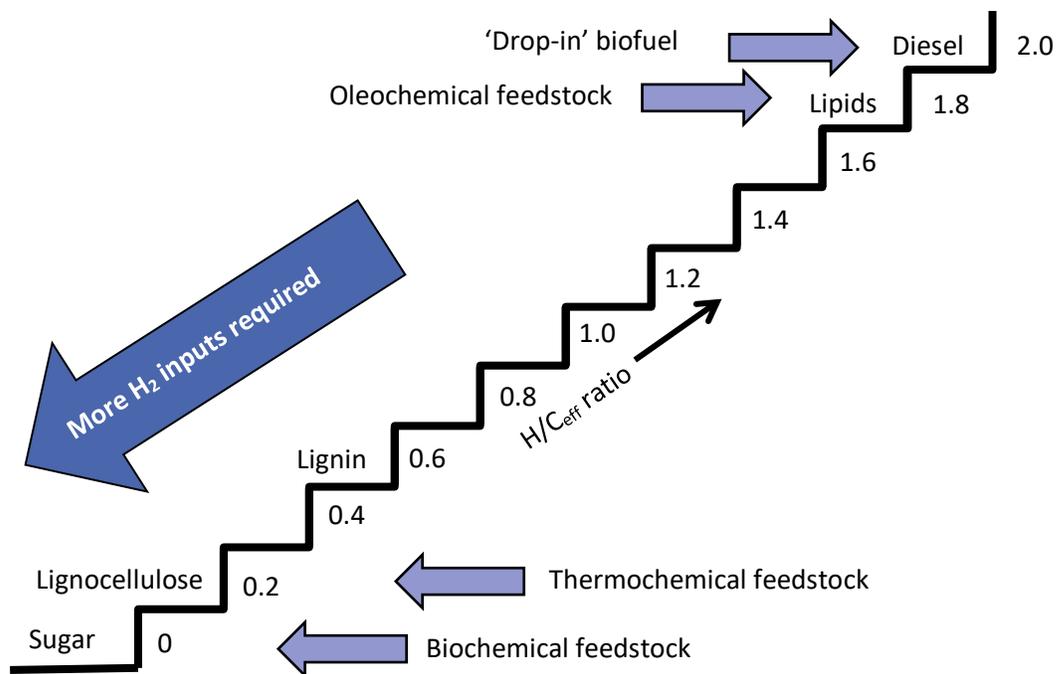
Figure 4 The effective Hydrogen to Carbon ratio "staircase"

Although the "staircase" and H_{eff}/C concept are useful "rules of thumb" that can help assess the suitability of "biomass materials" as feedstocks for drop-in biofuels, this concept may be oversimplified for biomass intermediates that are rich in both hydrogen and oxygen. For example, potential intermediates include mono-alcohols such as ethanol and butanol with a H_{eff}/C ratio of 2, which are still too oxygenated to be considered as drop-in biofuels. Other intermediates such as lignin ($H_{eff}/C=6$), although less oxygenated than sugars, are still several steps away from the drop-in H_{eff}/C target of 2. Typically, alcohol feedstocks have been used in routes such as the alcohol-to-jet fuel processes. Although the alcohols benefit from a high H_{eff}/C ratio they still need to be further deoxygenated (e.g. by using more hydrogen inputs) to produce hydrocarbons that are oxygen-free and suitable as drop-in biofuel blendstocks. It should also be noted that, if these alcohol and lignin feedstocks are derived from biomass, they will also require some type of pre-processing before they can be used.

Although a relatively simplified concept, the staircase model still illustrates that hydrogen inputs will be essential when upgrading bio-based feedstocks to drop-in biofuels, with some feedstocks requiring

significantly more hydrogen (sugars) than others (lipids). Consequently, hydrogen availability, sustainability and cost will play an important role in any future expansion of drop-in biofuel production and the "origins" of the hydrogen, whether fossil or renewable derived, will have a big impact on the carbon intensity of the finished fuels.

It should be noted that increasing demand for hydrogen is anticipated as hydrogen is already used to upgrade crude oil into finished fuels and for the production of ammonia. Consequently, the following section discusses current hydrogen production and use in the oil industry and the potential demand for hydrogen use during drop-in biofuel production.

1.3   CURRENT HYDROGEN USE AND PRODUCTION

As summarised earlier, the successful commercialization of drop-in biofuels will be heavily dependent on the availability and price of hydrogen (H_2) in order to elevate lipid and biomass H/C ratios. The current major global use of hydrogen is for petroleum refining and ammonia fertilizer production. Within the petroleum industry hydrogen is used to "decontaminate" (desulfurize and denitrogenize) crude oil and to upgrade ("crack") heavy oils to make "lighter" fuels. The declining quality of crude oil (e.g. higher sulfur), combined with stricter fuel regulations (lower sulfur emissions), has led to increased demand for hydrogen in the petroleum industry, intensifying future competition for this resource. The possible expansion of hydrogen-based fuel cells will place further constraints on hydrogen availability and cost.

When the US Energy Information Administration (EIA) summarised how the increased consumption of hydrogen had occurred in US refineries, it was apparent that the majority of refineries had opted to access external sourcing of hydrogen rather than expanding internal capacity (See Figure 5)[14].

U.S. refinery demand for hydrogen (2008–14)
billion cubic feet per day
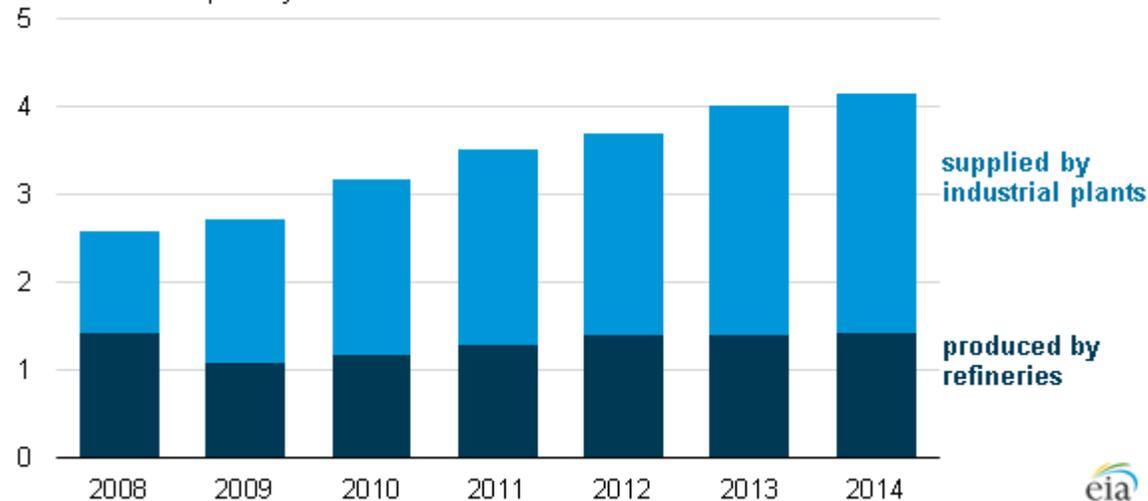
Figure 5 US Refinery demand for hydrogen (2008-2014) (billion cubic feet per day) ((EIA 2016))

1.3.1 Hydrogen demand for drop-in biofuel production processes

As mentioned in the previous section there will be increasing competition for hydrogen, with the oil refining industry needing it to produce higher quality products while the future drop-in biofuel sector will need it to upgrade and remove oxygen. In many cases external hydrogen will be required. For example, during the removal of oxygen and saturation of double bonds when using oleochemical feedstocks (lipids). For the removal of oxygen and hydrocracking for the case of pyrolysis biocrudes. When converting the double bonds in farnesene to farnesane and during the upgrading of Fischer-Tropsch liquids.

The upgrading of pyrolysis biocrudes is likely to be the process requiring the greatest amount of hydrogen for oxygen removal. As summarised in Table 1, when the Pacific Northwest National Laboratories (PNNL) compared the amount of hydrogen required to upgrade pyrolysis oils/hydrothermal liquefaction biocrudes with petroleum hydrodesulfurisation and petroleum hydrocracking, depending on the process, between 3 (single stage hydrocracking) and 75 times (naphtha hydrodesulfurisation) more hydrogen was required (Holladay 2014).

Table 1 Hydrogen (H₂) consumption for different processes (standard cubic feet/barrel) (Data: Holladay, PNNL) (HDO=hydrodeoxygenation, HDS=hydrodesulfurisation, ATM resid=atmospheric residue, HCK=hydrocracking)

Petroleum hydrodesulfurisation (HDS)				Petroleum hydrocracking (HCK)			Pyrolysis oil	HTL biocrude
Naphtha HDS	Kerosene HDS	ATM resid HDS	Gas Oil HDS	Mild HCK	Single Stage HCK	Resid HCK	HDO	HDO
45	**555**	**460**	**422**	**358**	**1150**	**660**	**~3400**	**~1800**

1.3.2 Hydrogen production and economics

At this point in time the main process used to produce hydrogen production is via the steam reforming of methane (SMR). As summarised below, the two main reactions that are involved in this conversion are:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \text{(water gas shift reaction)}$$
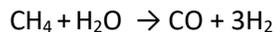
In the first reaction, methane reacts with high temperature steam to form syngas (CO and H_2). In the second reaction (also called the "water-gas shift" reaction) the CO reacts with steam to produce hydrogen and CO_2. Although methane, usually derived from natural gas, is the predominant feedstock because of its availability and relatively low cost, a variety of compounds, such as propane, methanol and many light gases, can be used to produce hydrogen in a steam reformer[15]. Refineries can also source hydrogen from the catalytic reformer, where aromatics are typically produced to increase the octane of fuel products[16]. Smaller gases from the crude feedstock can also be used in the steam reformer to produce hydrogen while excess hydrogen from hydrotreatment and hydrocracking units can be purified and recycled to provide hydrogen for upgrading.

In addition to steam reforming, alternative technologies for hydrogen production include electrolysis, partial oxidation and gasification (of oil, coal or biomass). In earlier work (Table 2), when Acar and Dincer (2014) compared the capital cost of different hydrogen production methods, steam methane reforming was found to have the lowest capital cost.

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[15] Neste has used propane, derived from hydrotreating of triglycerides, as a source of hydrogen in their refineries
[16] Co-processing of biobased feedstocks in the fluid catalytic cracker may result in higher aromatic formation in this reactor, and a lower hydrogen output from the catalytic reformer.

Table 2 Hydrogen production capital cost (Acar & Dincer (2014)).

Hydrogen production capital cost as a function of plant capacity (ton/day, tpd)	
Production technology	**Capital cost (million $)**
Steam methane reforming	$134 * (Capacity/150)^{0.75}$
Coal gasification	$352 * (Capacity/150)^{0.77}$
Biomass gasification	$360 * (Capacity/150)^{0.75}$
Water electrolysis	$598 * (Capacity/150)^{0.85}$

As mentioned earlier, the source of hydrogen is likely to have a significant impact on the carbon intensity of the fuels that are produced, with "green" sources of hydrogen being highly desirable. Although most work to date in the "renewable hydrogen" area has looked at the electrolysis of water, it can also be produced biologically. The most effective way of making hydrogen from biomass is to use gasification followed by steam reforming of the resulting syngas. However, this process is less than half as efficient (on an energy basis) as the conversion of natural gas to hydrogen, which can approach efficiencies of about 90%. In earlier work Holladay et al. (2009) reviewed the efficiencies of technologies related to hydrogen production from both fossil and renewable biomass resources. They concluded that the efficiency of natural gas steam methane reforming was excellent and that fossil-based technologies will continue to be more efficient than renewable hydrogen technologies for the foreseeable future. However, policies could play a significant role in driving production of renewable hydrogen through incentives such as awarding credits for lower carbon intensity of fuels or providing subsidies to facilitate the purchase of fuel cell vehicles[17]. Renewable hydrogen through electrolysis of water forms an important part of the Power to Liquid fuels section which is discussed later in this report (Section 5.4).

While the methane used in steam reforming is usually derived from natural gas, sometimes the refinery off-gases can also be used as a source of methane and CO to feed the hydrogen-producing reactions. Refineries that have limited access to natural gas may also gasify some of the residual crude oil cuts to make hydrogen. However, this is a highly energy intensive process and the use of a petroleum feedstock to make hydrogen as opposed to natural gas is unlikely in situations where there is a large difference between oil prices (high) and natural gas prices (low).

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[17] As found in California policies -https://www.afdc.energy.gov/fuels/laws/HY/CA

It is apparent that a key challenge that might limit the development drop-in biofuels will be finding cheap, sustainable sources of hydrogen. However, there is an opportunity to develop enhanced compatibility and leveraging opportunities with the current oil refinery infrastructure where, as described in the next section, several of the processes that will be needed to make drop-in biofuels already take place.

1.4   OIL REFINING AND DROP-IN BIOFUEL PRODUCTION

The processes involved in refining oil to fuels and chemicals have been developed and optimised for more than 150 years. Commercial drop-in biofuels production will involve many of the processes currently used in petroleum refining, including hydroprocessing (hydrotreatment and hydrocracking) and catalytic cracking. The earlier 2014 drop-in biofuels report provided a good, overall description of crude oil refining and processing units and the potential insertion points of bio-intermediates for co-processing. The reader is referred to the earlier report as the detailed description below builds on this earlier work.

1.5   CO-PROCESSING AND REFINERY INTEGRATION OF BIO-BASED FEEDSTOCKS – GENERAL CONSIDERATIONS

Many oil refineries have different configurations and target different products, including fuels, chemicals, asphalt, etc. Consequently, they may be more-or-less able to provide suitable insertion points for the various bio-intermediates, depending on the nature of the intermediate and the desired products as summarised in the "generic", hypothetical refinery configuration depicted below.
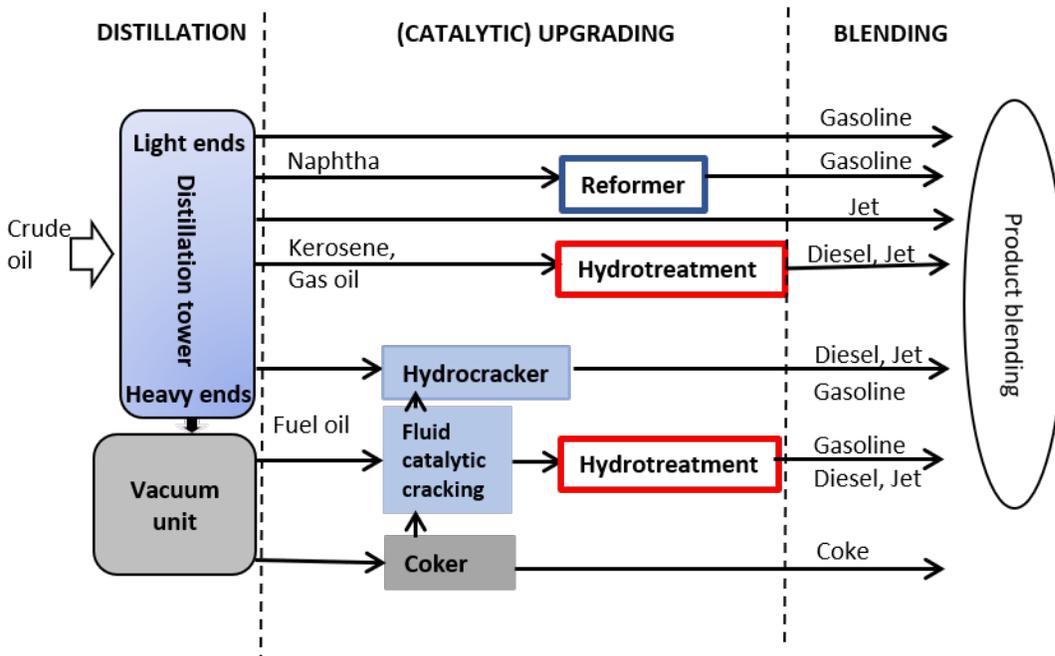
Figure 6 Simplified diagram of an oil refinery. (Karatzos et al. 2014)

It is likely that many of the biocrudes that might be upgraded at a refinery will contain large molecules. Consequently, some form of cracking will be required to create shorter molecules that comply with the specifications for specific fuels. This could take place in one or more of the three processing units which include, the fluid catalytic cracker, the hydrocracker or the delayed coker (thermal cracking). Typically, hetero-atoms are removed through hydrotreating, while processes such as isomerization, catalytic reforming and alkylation are typically used for final polishing steps.

A recent review by PNNL described which US refineries, based on configuration, could be better suited to "biorefinery integration" (Freeman et al. 2013). This work indicated that two characteristics are important in a refinery integrated with biobased intermediates. Namely, processes that convert large molecules into smaller molecules (cracking, with or without hydrogen), and processes that remove oxygen, primarily done through hydrotreating. These workers concluded that refineries that have no hydrotreating are unsuitable for upgrading of bio feedstocks unless oxygen removal was carried out prior to insertion. (Freeman et al. 2013). As will be discussed in more detail in the following section and summarised in Table 3, potential insertion points and processing needs will be determined based on the targeted products and the upgrading needs when dealing with different feedstocks and various technologies.

Table 3 Characteristics of different bio-intermediates and main refinery requirements. (Huber et al. 2006; Lamprecht et al. 2007; Kamara and Coetzee 2009; Biller and Roth 2017; Griffin et al. 2018; Karatzos et al. 2014)

	Characteristics	Refinery needs
Vegetable oils	Triglycerides and free fatty acids Some heterogeneity with respect to chain length of fatty acids, but chemically quite homogenous Lipids in diesel range 11% oxygen, 1.8 H/effC ratio Waste oils have higher free fatty acids which affects the acidity. Waste oils also have other contaminants Metals/inorganic compounds	Removal of oxygen Some cracking may be required for specific products such as jet fuel as lipids in diesel range Isomerization/branching to improve cold-flow properties (biojet) Needs the least upgrading Fractionation may be required after cracking
Pyrolysis bio-oils	Up to 400 different components High oxygen levels over 40% Variable aromatic content from degradation of lignin Water content Catalytic pyrolysis oils or partially hydrotreated pyrolysis bio-oils have lower oxygen levels than bio-oil (for catalytic pyrolysis oil, the oxygen content is generally between 18-24 wt%)	Removal of oxygen Thermal or catalytic cracking of large molecules into smaller molecules Potential hydrocracking of aromatics Fractionation into different products after upgrading
HTL biocrudes	Lower oxygen content (range: 6-18%) Lower water content	Oxygen removal Cracking of larger molecules Hydrocracking of aromatics
FT liquids	High temp FT creates smaller molecules suitable for gasoline Low temp FT creates longer molecules in the diesel range	Fractionation required May require cracking & Isomerization

1.5.1 Evaluation of insertion points

As summarised below, there are a number of potential insertion points for bio-intermediates in various refinery processes (Figure 7). However, the potential risk to the refiner will play a significant role in the final selection of the insertion point, with the blending of the biobased fuels and petroleum fuels as finished fuels likely the lowest risk option, while insertion at the predistillation phase posing the greatest risk.
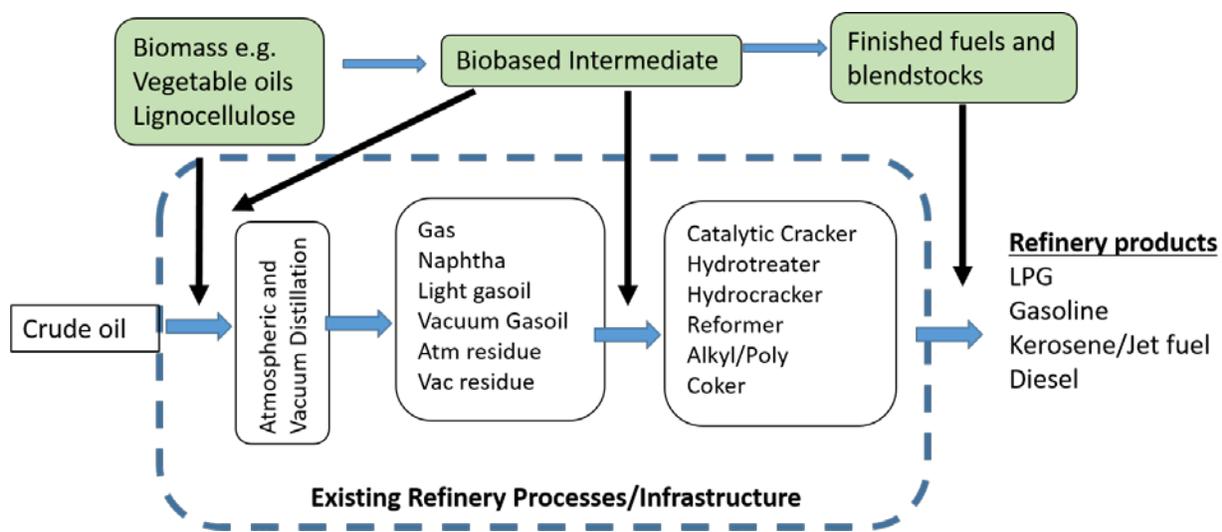
Figure 7 Potential refinery insertion points for bio-intermediates (based on Holladay (2014)).

1.5.2 Distillation as an insertion point for biobased intermediates

Unless the biobased intermediates are functionally equivalent to crude oil, several problems can arise when trying to upgrade them by insertion at the distillation stage. For example, any biobased intermediate that might contain a contaminant could result in the contaminant being distributed throughout the refinery. Any biobased intermediate which is inserted at this stage of the refinery will have to be virtually free of oxygen and free of possible contaminating and reactive species such as olefins, carbonyls, alcohols and aldehydes. An additional problem is the unstable nature of biobased intermediates at increased temperatures. Heating resulting in an increase in polymerisation as the compounds react with each other, leading to increased viscosity and increased residue formation. Many bio-oils/biocrudes also contain significant amounts of non-volatile compounds such as sugars and oligomeric phenolics which impede distillation.

1.5.3 Fluid Catalytic Cracker (FCC) as insertion point

The fluid catalytic cracking (FCC) unit is typically used to "crack" heavy molecules (the usual feed is heavy gas oil, vacuum gas oil or residues) and is typically the main process used to produce gasoline (50%) and propylene. (Vogt and Weckhuysen 2015) The FCC insertion point should be economically attractive as no external hydrogen is required and FCC catalysts are more tolerant than hydroprocessing catalysts to higher oxygen levels in the biofeeds. (Agblevor et al. 2012) Another benefit is that FCC catalysts, usually zeolite catalysts in a silica or alumina matrix, are continuously regenerated on-site by burning off any coke deposits in a regenerator attached to the FCC unit before recirculating the catalyst. The regeneration and combustion of coke produces heat which can be used in the refinery. However, excess coke production resulting from the insertion of biobased feeds could cause unacceptable increases in temperature that could cause damage to the FCC catalyst, posing a challenge to appropriate heat balance maintenance (Fogassy et al. 2011; Al-Sabawi et al. 2012; Talmadge et al. 2014). It is also recognised that acid-catalysed cracking occurs in the FCC, with additional thermal cracking of larger molecules taking place outside the catalyst due to the high temperatures that are generated. The general characteristics of catalytic cracking are that the largest molecules get cracked first, olefins are formed and the alkyl chains attached to aromatic rings are then cleaved off if they have three or more carbons (Jones and Pujadó 2006). Secondary reactions, involving polymerisation and condensation, also take place and these contribute to formation of coke. It should be noted that aromatics do not undergo any cracking in an FCC and that any potential insertion of pyrolysis bio-oils into the FCC will likely result in a greater aromatic content in the products (Pinho et al. 2015).

A key consideration when assessing catalytic cracking as a possible co-processing insertion point is the experimental set-up and how much this truly represents an industrial process. As was recently highlighted by Bezergianni and co-authors (Bezergianni et al. 2018), "the choice of reactor type is a crucial factor to be considered when evaluating the prospects of the bio-oil co-processing and evaluating the product selectivities. Pilot and demo-scale FCC units similar to real industrial FCC units are clearly a better choice to carry out experiments when studying bio-oil co-processing with petroleum fractions." These researchers (Bezergianni et al. 2018) described various configurations including the micro activity test (MAT) reactor, Advanced Catalyst Evaluation (ACE), laboratory scale micro-risers and laboratory scale two-stage riser fluid catalytic cracking unit, as well as pilot plants. Many of these options have been used for both catalyst evaluation and to assess reactor behaviour and product formation based on different feedstocks. However, the authors point out several shortcomings of these options, such as the fixed bed

MAT reactors not being steady state processes and the contact time between catalyst and feedstock being 10-100 seconds whereas in commercial FCC's it would be 1 second. This shorter time enhances hydrogen transfer reactions and has an impact on the products formed. Related work by de Rezende Pinho et al (2015, 2017), showed that these experimental set-ups generally resulted in higher coke formation than in a more realistic set-up that mimics commercial scale FCCs. While these workers concluded that these experiments helped us better understand possible co-processing of bio feedstock options, it also indicated the limitations of some of the work to accurately predict product distribution (coke vs liquid products).

Fluid catalytic cracking capacity is closely linked with demand for gasoline, thus it is more common in North American refineries where there is a higher demand for gasoline. In contrast, refineries in Europe have a higher demand for diesel which is typically produced through hydrotreating/hydrocracking. (Cooper 2017; OPEC 2017)

1.5.4 The Hydrotreater as an insertion point

Hydrotreating is primarily used in petroleum refineries to remove heteroatoms from petroleum product streams. The process involves higher temperatures and pressures as well as specialized catalysts. Hydrocracking is more severe and requires specialised bifunctional catalysts. (Uner 2017; Jones and Pujadó 2006). Hydrotreating reactions will generally proceed in the following order, (organometallic) metals removal, olefin saturation, sulfur removal, nitrogen removal, oxygen removal and finally halide removal (Jones and Pujadó 2006). Although some aromatic saturation will take place, this will be limited as ring opening requires special catalysts and higher operating pressures.

Hydrotreating reactors are mostly fixed catalyst beds, with cobalt and molybdenum sulfide on alumina catalysts most often used. Other catalysts that have been used include nickel sulfide, nickel thiomolybdate, tungsten and nickel sulfides and vanadium oxide (Karatzos et al. 2014). Typically, catalysts are regenerated at an off-site facility after months or years (cycle can be 12 months to 60 months) of operation as replacement of catalyst may be costly (Robinson 2006). The absence of in situ regeneration, as occurs with the FCC catalysts, mean that the hydrotreater is less tolerant to contaminants. Thus, deactivation and the risks associated with insertion of unknown feeds are much greater.

Hydrotreating is an exothermic reaction, with the heat released proportional to the consumption of hydrogen (Jones and Pujadó 2006; Elliott 2007; Jęczmionek and Porzycka-Semczuk 2014). Thus, as

discussed earlier, oxygen removal generates significant heat and temperature in the reactor and has to be controlled to prevent unwanted reactions taking place which can result in increased coking, a decrease in pressure or poor liquid flow distribution (Egeberg et al. 2010; Egeberg et al. 2011). It should be noted that sulfur and nitrogen occur at relatively low concentrations in crude oil as compared to the potential high concentrations of oxygen in biobased intermediates. As summarised in Table 4, there are significant composition differences between biobased feedstocks and crude oil.

Table 4 Comparison of typical composition of various biobased feedstocks with crude oil. (Jensen et al. 2017; Holmgren et al. 2007; Mortensen et al. 2011; Passikallio 2016)

	Vegetable oil[1]	Fast pyrolysis[2]	Catalytic fast pyrolysis[3]	Hydrothermal liquefaction[4]	Crude oil[2]
C, wt%	77.6	55-65	72	81.4	83-86
O, wt%	10.4	28-40	21.5	9.8	<1
H, wt%	11.7	5-7	6.4	8.7	11-14
S, wt%	0.0006	<0.05	--	0.01	<4
N, wt%	0.0011	<0.4	0.02	0.095	<1

[1] Data taken from Holmgren et al. 2007 using soybean oil.
[2] Data taken from Mortensen et al. 2011.
[3] Data taken from Passikallio 2016.
[4] Data taken from Jensen et al. 2017.

Consequently, although the processes used for sulfur, nitrogen and oxygen removal are similar, more hydrogen will be required to remove the oxygen and the catalysts that are most suitable for removing sulfur and nitrogen may not be optimal for removing oxygen. Even at high hydrogen pressures the removal of oxygen will not exclusively proceed through hydrogen addition as CO and CO_2 will also be formed. These products can also cause inhibition of catalysts and, since regeneration does not take place in situ, can cause significant problems for the refinery.

1.5.5 Hydrocracking as an insertion point

Hydrocracking involves the reduction of large molecular weight compounds into lower molecular weight products, while adding hydrogen and carrying out similar reactions to those described previously for hydrotreating. This is done in the presence of hydrogen and at high pressures (around 2,000 psig/14 MPa). (Karatzos et al. 2014) Although hydrocracking is costly, the resulting products require less downstream processing. It should be noted that hydrocracking reactors are not suitable for feedstocks containing oxygen or other impurities unless the feeds have first been hydrotreated. The high cost of catalyst and offsite generation make this process very sensitive to any contamination. Thus, hydrocracking may be used as a second step in upgrading of biobased feedstocks where size reduction is still required.

1.5.6 Fate of renewable carbon

Policies such as British Columbia's low carbon fuel standard[18] which, among other things, promotes biofuels consumption, need to account for the renewable content of the fuel to determine its carbon intensity. These types of policies will play an increasingly important role in promoting the willingness of refineries to co-process bio-oils/biocrudes. However, it also means that we will have to better determine the carbon intensity of a fuel using tools such as life cycle assessment (LCA).

At this point in time, the California Air Resources Board (CARB) is considering including co-processing pathways within their Low Carbon Fuel Standard (CARB 2017). One of the key issues which is under consideration is how to quantify the renewable content of a fuel and the corresponding credits that can be earned by obligated parties. The methods currently under consideration include the ^{14}C isotopic method, mass balance based on observed yields, and the carbon mass balance method (CARB 2017).

To date the ^{14}C isotopic approach has been the predominant research method used to track renewable content. (Fogassy et al. 2012; Wang et al. 2016; Pinho et al. 2015, 2017) However, it is expensive and time-consuming and there are ongoing concerns related to the absolute error of the methodology, especially for low percentage co-processing (CARB 2017). Existing biofuel producers such as the Renewable Energy Group (REG) and companies represented by the National Biodiesel Board have stated that both the mass

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[18] https://www2.gov.bc.ca/gov/content/industry/electricity-alternative-energy/transportation-energies/renewable-low-carbon-fuels

balance method, based on observed yields, or carbon mass balance method are inadequate, as neither provides verifiable quantification that could be used to ensure renewable content in the fuels (Scott 2017; REG 2017).

While the main focus of this report is on liquid fuels, renewable content of the final product may also end up in the solid or gaseous phase. Consequently, consideration should also be given to how decarbonisation of these products might also be included. For example, using renewable coke products to generate heat may reduce the emissions related to fuel production (as opposed to combustion where a baseline value for a fuel is used).

Another impact of co-processing is the regulatory environment around fuels and fuel specifications which will have to be adapted to accommodate the inclusion of renewables. This has particular significance for the aviation sector as biojet fuels go through a lengthy and expensive process to become certified under ASTM D7655. The insertion of biobased intermediates in a refinery producing a range of lower carbon fuels will likely produce a jet fuel fraction with a lower carbon intensity. However, unless an ASTM standard has been approved for co-processed jet fuel, it will not meet specifications. Currently, an application for certification of co-processed vegetable oil jet fuel has been approved based on 5 vol% insertion of vegetable oil with middle distillates in hydroprocessing. The certification is based on compliance with D7566 (of HEFA) and is further explained in the latest standard specification for aviation turbine fuels (D1655-18a)[19].

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2. THE OLEOCHEMICAL PLATFORM

The oleochemical pathway has been the only significant source of commercial "drop-in" biofuel production to date and this will likely continue to be the case in the short to medium term as other drop-in biofuel technologies develop. Current production capacity is about 5 BL and is based on lipid feedstocks such as vegetable oils or other bio-derived fats such as tallow, used cooking oils and tall oil. These lipid based feedstocks have "pioneered" the drop-in biofuels area as they are the "easiest" to upgrade to finished fuels, primarily due to low amounts of oxygen (11%) and a high hydrogen-to-carbon (H_{eff}/C) ratio (1.8:1) (See the hydrogen staircase in Figure 4). The most common lipid based biofuel that is used to date is "biodiesel" which is produced via esterification of triacyl glycerides (TAGs) to produce fatty acid methyl esters (FAME). However, FAME/biodiesel is not a drop-in fuel and a deoxygenation step is required to convert lipids into the drop-in biofuel commonly known as renewable diesel. This is mainly carried out through a hydroprocessing step and the biofuel are typically known as hydrotreated esters and fatty acids (HEFA) or hydrotreated vegetable oils (HVO). This hydrogen-requiring process represents the only route to date that has been able to deliver commercially meaningful amounts of drop-in biofuels and these feedstocks are main source of the biojet fuels that used currently used in aviation.

2.1 PROCESS OVERVIEW

Hydroprocessed Esters and Fatty Acids (HEFA) is the term used to describe advanced oleochemical drop-in biofuels that are produced by hydrotreating lipids derived from vegetable oils, algae and animal fats. To distinguish HEFA from "FAME biodiesel", the terms "green diesel" or "renewable diesel" are often used. Alternative acronyms for HEFA renewable fuels include HDRD (hydrogenation derived renewable diesel), HRV (Hydrotreated Renewable Vegetable oils), HVO (Hydrotreated Vegetable Oils) and HRO (Hydrotreated Renewable Oils). Other common acronyms used to describe the type of HEFA ASTM certified for use in blends with jet fuels are HRJ (Hydrotreated Renewable Jet fuel) and HEFA-SPK (synthetic paraffinic kerosene). Biodiesel itself has limited compatibility with petroleum in pipelines and there is the potential of contaminating jet fuels if they are transported in the same pipeline. Earlier jet fuel specifications were very stringent permitting only 5 ppm of FAME contamination in jet fuel. However,

in 2015 after extensive testing, ASTM agreed to increase this minimum FAME to 50 ppm[20] and this might be further increased to 100 ppm in the future.

Compared to other potential biofuel feedstocks such as sugars and cellulosic biomass, fats are the simplest to convert to drop-in biofuels because as they have a lower oxygen content and their chemistry is closer to a hydrocarbon than saccharides or lignins (i.e., their effective hydrogen to carbon ratio is closer to 2). Despite these benefits, the conversion of fats to HEFA entails significant capital costs as well as hydrogen inputs when compared biodiesel (FAME) production.

In a standalone facility, HEFA is typically produced in two stages (Figure 8). During the first stage, the fats are deoxygenated and their double bonds are saturated to create alkanes. The second stage involves alkane isomerisation and cracking to improve the cold flow properties and produce a jet fuel fraction. It should be noted that not all facilities use cracking/isomerisation unless biojet fuel is produced. Isomerisation is used to make winter and arctic diesel based on market demand in cold climates and is not carried out by all companies. As cracking may result in smaller molecules of less value, conditions in the second stage are generally controlled to minimise cracking.
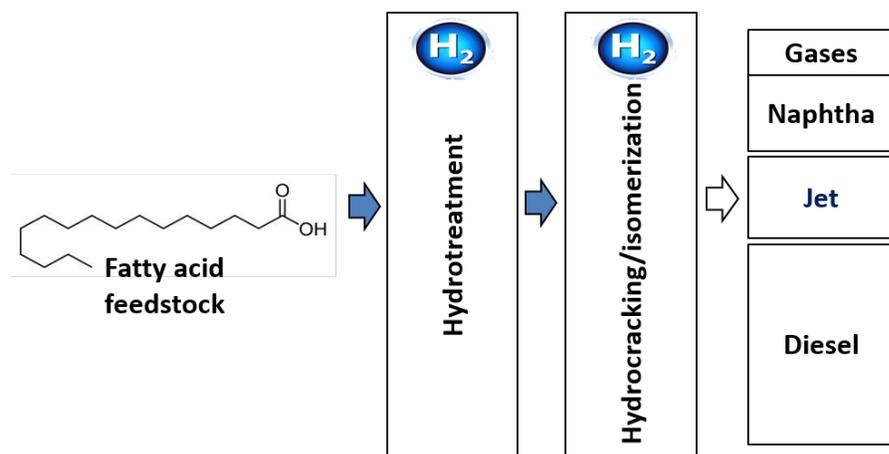
Figure 8 Simplified Hydroprocessed Esters and Fatty Acids (HEFA) process depicting the 2 stages of hydroprocessing

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[20] http://www.greenaironline.com/news.php?viewStory=2048

Several chemical reactions take place during HEFA production, with the carbon-carbon double bonds present in the triacyl glyceride (TAG) saturated first. This is followed by the removal of the propane backbone within the TAG leaving 3 free fatty acids per TAG molecule. Finally, the fatty acids are deoxygenated through three reactions, hydrodeoxygenation (where oxygen leaves as H_2O), decarboxylation (where oxygen leaves as CO_2) and decarbonylation (where oxygen leaves as CO and H_2O) resulting in the formation of alkyl chains (Refer to section 1.2 for more details). During hydrodeoxygenation (HDO) the alkyl chain length is typically preserved whereas during decarboxylation (DCO) the alkyl chains are shortened due to the loss of a carbon atom as CO_2. A combination of the two deoxygenation reactions usually take place in commercial hydrotreating facilities even with addition of hydrogen (as described in section 1.2). The ratio of these deoxygenation pathway reactions (typically HDO/DCO = 35/65) is important in hydrotreating operations as it determines hydrogen consumption, product yields, catalyst inhibition, gas consumption and heat balance (Egeberg et al. 2010). It should be noted that the "tuning" of the deoxygenation pathway ratio can be achieved via catalyst adjustment, depending on the strategic manufacturing priorities as well as the feedstock and hydrogen costs and the value of the fuel product or blendstock being produced. For example, the UOP-Honeywell facility opts for more decarboxylation in order to reduce capital costs while Syntroleum prioritises the preservation of longer carbon chains (higher product quality) and thus uses more hydrodeoxygenation (Pearlson 2011).

After the first processing stage, the TAG feedstock has been converted to an oxygen-free, saturated liquid alkane intermediate. This hydrocarbon liquid can be directly blended with petroleum diesel. However, as it is comprised of straight alkane chains, it has poor cold flow properties. To produce a product with better cold-flow properties, a second stage is often added where the unbranched long chain alkanes are cracked and isomerised using catalysts (Pearlson 2011). Isomerisation increases the branching of the carbon chains, thereby reducing the freezing point of the resulting finished fuel. If HEFA-jet is the desired product, the conditions used will be more severe to promote cracking, so that a greater number of molecules fall within the jet range (C8-C16). However, this will result in a loss of liquid fuel product yield through the formation of smaller molecules.

The mass yield of HEFA liquids from lipid raw material is typically around 80% but varies according to the feedstock and processing conditions used (Sotelo-Boyás et al. 2012; Pearlson 2011). The remaining 20% of material is generally composed of light gases such as propane, methane and oxygenated gases such as CO_2 and CO. Other than CO_2, these gases can be combusted to provide power for the process or used as

feedstocks in the steam reforming unit to generate hydrogen. Typical HEFA liquids comprise 3 different fractions corresponding to jet, diesel and naphtha blendstocks. The distribution of these three liquid product fractions can be controlled by changing the reaction conditions and catalysts. However, diesel generally predominates with only a small portion of the liquids in the jet range (Bezergianni et al. 2009; Pearlson 2011). It has been reported that the UOP-based HEFA process (maximum decarboxylation), resulted in ca. 65 wt% of the incoming vegetable oil converted to diesel-range molecules and only ca. 13 wt% to jet-range. Increasing the jet yield to 50 wt% requires 30% more hydrogen and reduces the overall liquid fuel yield of the process from 80 wt% to about 70 wt% (Pearlson, 2011). The extra processing required to maximize jet fuel production imposes extra economic and logistic challenges and jet fuel does not generally command a higher price than diesel. Targeting maximum jet fuel production is therefore not good economics and facilities such as World Energy (previously AltAir Fuels) does not target maximum jet fuel but produce both diesel and jet. In the absence of a price premium for jet fuels compared to diesel fuels, the jet fraction is included within a wider-cut diesel range. It would be difficult to justify the extra cost of maximizing HEFA jet yields and the cost of separating jet from diesel fractions unless there is significant price premium for HEFA jet fuel compared to HEFA diesel.

Policy will also play an important role in this regard. Where incentives are available for renewable diesel, but not for biojet fuels, oleochemical feedstocks would be preferentially targeted to making renewable diesel to access the incentives. In order to promote biojet fuel production, a separate biojet incentive could be provided to drive jet production. It should be noted that, although HEFA diesel and jet compete for the same feedstock, in practice, both biofuels are made simultaneously.

2.2 FUEL QUALITY

The process of hydrotreating vegetable oils can result in the production of high quality HEFA fuels that exceed the specifications of petroleum-based transportation fuels. As an example, HEFA derived diesel and jet fuel have essentially no sulfur content whereas their petroleum counterparts can contain up to 3000 ppm of sulfur. Other improved characteristics of HEFA fuels include higher energy density, lower aromatics content and, for diesel HEFAs, higher cetane number (Table 5).

Table 5 Selected properties and specifications of fossil and renewable HEFA diesel and jet fuels.

Property		Diesel		Jet	
		Fossil	[1]HEFA	Fossil	[2]HEFA
Oxygen content	wt %	0	0	0	0
Specific gravity	kg/L	0.84	0.78	0.75-0.84	0.73-0.77
Cetane		40-52	70-90	-	-
Sulphur	ppm	<10	<2	<3000	<15
Specific energy	MJ/kg	43	44	>42.8	44.1 (typical)
Aromatics	Vol %	<12	0	<25	<0.5

[1]Properties of renewable diesel from UOP Green Diesel. [2]ASTM D7566 Annex 1 used for hydroprocessed renewable jet specification. Source: (Pearlson, 2011)

The absence of aromatics in renewable HEFA is generally viewed as an advantage from an air pollution perspective since phenolic compounds are associated with emissions of polyaromatic hydrocarbon (PAH) pollutants (European Commission 2001). While aromatics are generally undesirable in petroleum fuels, a minimum amount is required to meet aviation fuel specifications as low levels of aromatics are needed to swell the seal elastomers in an aeroplane engine's fuel system. The absence of aromatics in HEFA means that these "drop-in" biofuels will likely be used as blendstocks that need to be blended with petroleum jet fuel. This is one of the reasons why the ASTM standards have only approved 50% blends of HEFA biofuels for jet use (Bauen et al. 2009; Hileman et al. 2009).

2.3 IMPACT OF FEEDSTOCK CHARACTERISTICS ON FUEL PRODUCTION

As mentioned earlier, the chain length of the fatty acids in the triacyl glyceride (TAG) feedstock will have an impact on the products of a HEFA facility. Most of the feedstocks available today are derived from vegetable oils and they typically contain long fatty acid chains equivalent to the carbon chain length of diesel i.e. C_{16}-C_{22}. Although these molecules can be cracked to shorter chains to fit the "lighter" jet fuel and gasoline range, the cracking step is not sufficiently selective, creating smaller gases as by-products and reduces the overall liquid fuel yield. For example, when a long alkyl chain is cracked, only some of the chains are of the desirable length while a number of undesirable short chains are also produced. These "too-short" chains form a light naphtha-like byproduct and the overall fuel yield is reduced. Some oils, such as those derived from coconut, palm kernels and most cyanophyta, contain TAGs with shorter chain fatty acids (which are in the jet fuel range) (Bauen et al. 2009; Pearlson, 2011), making them more suitable for biojet production. However, these feedstocks are currently only available in relatively small volumes

with cyanophyta oils currently only produced in small volumes. In 2017/18, only about 8.31 million metric tonnes of palm kernel oil (not to be confused with palm oil) were produced annually compared to the global 197.95 million metric tonnes of vegetable oils that are produced annually[21].

The number of double bonds in a vegetable oil feedstock will also have an impact on the volume of hydrogen required to saturate these bonds and this will consequently impact overall processing cost. However, feedstocks such as tallow and palm oil already contain high levels of saturated hydrocarbons and should thus be "cheaper" to upgrade.

Tall oils, which are also considered to be an oleochemical feedstock, are a by-product of pulp mills and they are mainly derived from the resins and extractives present in softwood feedstocks such as pine, spruce and birch. Due to being primarily comprised of large amounts of resin acids and free fatty acids they are very acidic. To improve transport logistics tall oils are typically processed to methyl esters prior to shipping from the pulp mill. The resulting tall oil derived FAME liquids are known by the abbreviation RTD (raw tall diesel). The Preem AB oil refinery in Gotenburg, Sweden developed and demonstrated the ability to hydrotreat up to 30% RTD blends with 70% mineral oil in a conventional refinery (Egeberg et al., 2010) with Haldor Topsoe providing the catalyst beds and process design. Hydrotreating FAMEs (such as RTD) is slightly different from hydrotreating vegetable oil TAGs. The major difference is that a high yield of by-product methane is obtained when processing FAMEs as compared to the predominant propane that is produced when processing TAGs.

2.4   COMMERCIAL PRODUCTION VOLUMES AND FACILITIES

As mentioned earlier, oleochemical derived biofuels are the only drop-in biofuels that are being produced at a fully commercial scale today with HEFA renewable diesel production capacity exceeding 5 BL (Table 6). Production is dominated by Neste, a Finnish petroleum refining company, that is currently the world's largest producer of drop-in biofuels and which operates 4 HEFA facilities (2xFinland, Rotterdam, Singapore). Companies employing the UOP/Eni Ecofining™ technology with significant production are Eni in Italy, Diamond Green Diesel (joint venture of Valero and Darling) in Louisiana, and World Energy (formerly AltAir Fuels) in California. Although World Energy commenced production in 2017 as a "HEFA/

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[21] https://apps.fas.usda.gov/psdonline/circulars/oilseeds.pdf

biojet facility", renewable diesel is the largest volume product coming out of this facility. The Renewable Energy Group (REG) employs a third technology, Biosynfining®[22].

Although several companies such as Neste initially used significant volumes of palm oil as a feedstock, most companies have switched to increased amounts of waste feedstocks such as used cooking oil. Neste claims that waste oils currently constitute up 80% of their feedstock[23]. For more information on the various plants that are operating, the IEA Bioenergy Task 39 Advanced Demonstration plant database (http://demoplants.bioenergy2020.eu/) can be consulted.

All of the current HEFA facilities make HEFA renewable diesel with the exception of World Energy, which makes both HEFA renewable diesel and HEFA-jet fuels. Current policies and economics favour the production of renewable (HEFA) diesel as incentives can be earned for renewable diesel under legislation such as the US Renewable Fuel Standard, while specific incentives are not currently available for biojet fuels.

An ASTM application for approval of HEFA+ (a term used by Neste) to be used as an aviation biofuel, has been launched by Neste and Boeing. HEFA+ is essentially a renewable diesel with good cold-flow properties. If this ASTM application is approved, the potential biojet fuel available for aviation use would be greatly expanded as any oleochemical-based HEFA renewable diesel could then be blended into fossil jet fuel. Boeing carried out a test flight using a 15% blend of green diesel[24] and Neste's website indicated that a winter grade green diesel was used for this demonstration[25].

Table 6 Facilities producing drop-in biofuels, mainly renewable diesel, based on the oleochemical platform.

Company	Location	Feedstock	Capacity
Neste	Rotterdam	Vegetable oil, UCO and animal fat	1.28 bn L/y
Neste	Singapore	Vegetable oil, UCO and animal fat	1.28 bn L/y
Neste	Porvoo, Finland	Vegetable oil, UCO and animal fat	385 m L/y
Neste	Porvoo 2, Finland	Vegetable oil, UCO and animal fat	385 m L/y
ENI	Venice, Italy	Vegetable oils	462 m L/y
Diamond Green Diesel	Norco, Louisiana	Vegetable oils, animal fats and UCO	1.04 bn L/y
UPM	Lappeenranta, Finland	Crude tall oil	120 m L/y
AltAir	Paramount, California	Non-edible oils and waste	150 m L/y
Renewable Energy Group	Geismar, Louisiana	High and low free fatty acid feedstocks	284 m L/y
Total (start-up)	La Mède	UCO and vegetable oils	641 m L/y
Emerald Biofuels(under construction)	Port Arthur, Texas	Vegetable oils	416 m L/y

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[22] http://www.regfuel.com/technologies/bio-synfining
[23] https://www.neste.com/en/companies/products/renewable-fuels/renewable-raw-materials
[24] https://fuelsandlubes.com/fli-article/boeing-completes-test-flight-with-15-green-diesel-blend/
[25] https://www.neste.com/na/en/customers/products/renewable-products/nexbtl-renewable-aviation-fuel-0

2.5 POTENTIAL FOR INTEGRATION WITH OIL REFINERIES

Although a variety of oleochemicals/lipids can be used to produce drop-in biofuels the differences in the chemical characteristics of the feedstock such as the chain length of fatty acids, degree of unsaturation, free fatty acid content and the possible presence of contaminants will all influence their upgrading to drop-in biofuels. Processes such as hydrotreating are more flexible with respect to the free fatty acid content of the various oleochemical feedstocks than are the traditional processes used to produce biodiesel (fatty acid methyl esters). However, the main consideration from an engineering perspective is the acid or total acid number (TAN) levels of the feedstock as feedstocks with a high free fatty acid content will likely require more expensive metallurgy to prevent corrosion (Marker 2005).

2.5.1 Possible insertion of lipids in hydrotreaters

As mentioned earlier, the upgrading of triglycerides take place in multiple stages with the double bonds on the fatty acid chains first hydrogenated, followed by the formation of fatty acids and propylene with the propylene typically converted to propane, using hydrogen and high pressures. This is finally followed by the deoxygenation of the fatty acids through hydrodeoxygenation, decarboxylation and decarbonylation (Jęczmionek and Porzycka-Semczuk 2014). One potential concern with co-processing vegetable oils with petroleum liquids is how it might impact desulfurization as greater volumes of hydrogen will likely be required (Donnis et al. 2009; Al-Sabawi et al. 2012).

However, conflicting reports in the literature indicate that this is not a simple matter as reduced hydrodesulfurization and hydrodenitrogenation was found for conventional CoMo-type catalysts, but not for NiMo catalysts (Bezergianni et al. 2014; Egeberg et al. 2010). Other work (Lappas et al. 2009) also found that hydrocracking was inhibited when vacuum gas oil and sunflower oil were co-processed. However, some studies have shown that hydrotreating of vegetable oils with a petroleum-based feed did not impact hydrodesulfurisation (Chen et al. 2013; Huber et al. 2007; Rana et al. 2013) and actually improved the yield of alkanes when compared to hydrotreatment of vegetable oils alone (Huber et al. 2007).

Recently, Bezergianni et al. (2018) suggested that these variable results were partly due to the specific fossil feedstock used during co-processing as well as the nature of the renewable feedstock (chain length,

degree of saturation), blending level and reactor conditions. Some general trends highlighted by Bezergianni et al. (2018) include:

- Low quality feedstocks containing water and a high fatty acid content may require pretreatment prior to insertion into the hydrotreater;
- Above a 15% feed, lower liquid yield and sulfur removal resulted. An optimum ratio of 10% vegetable oils was recommended;
- Higher H_2 pressures are required for co-processing of vegetable oils. However this could cause some cracking to occur;
- Some studies indicate that saturated lipids could be hydrotreated at lower temp (320-340℃) than unsaturated lipids (over 340℃);
- A higher H_2 to oil ratio favours saturation and heteroatom removal. However, this depends on the saturation level of the bio-feedstock (palm oil and tallow are more saturated);
- Compared to CoMo and NiW catalysts, NiMo catalysts are usually better for lipid co-processing as they show lower deactivation rates while the hydrodesulfurisation and hydrodenitrogenation reactions are not affected.

Despite these challenges, as demonstrated by Preem, Cepsa, Repsol and Kern Oil, hydroprocessing is the only type of co-processing that has reached full commercial scale. (Hinds 2017; Greenea 2017) However, for the types of reasons mentioned earlier, co-hydroprocessing using oleochemical feedstocks will likely remain challenging. As an alternative, standalone hydroprocessing units co-located at existing refineries might prove more attractive, even though the initial capital costs are higher. (Melero et al. 2012; Greenea 2017) The primary reason is because the purer, higher value products (renewable diesel, renewable jet, renewable gasoline and renewable propane) that will be produced will provide the refiner increased flexibility to either blend with other low-grade streams or sell directly as drop-in biofuels (Greenea 2017).

Although co-hydroprocessing of oleochemicals may not be suitable for every refiner, as additional equipment may be needed and operational cost will probably be higher, it is still likely that this is where co-processing will first be developed at a commercial level.

2.5.2 Insertion of lipids in the fluid catalytic cracker

As most studies have focused on co-processing in the hydrotreater or in standalone hydrotreatment only limited information has been published on the co-processing of vegetable oils and lipids in the fluid catalytic cracker (FCC). However, it is likely that co-processing of lipids in the FCC will be advantageous as potential synergies between the lipids and the fossil feed can result in increased conversion and increased octane number of the products as well as enhanced oxidative stability (Doronin et al. 2013; Bezergianni et al. 2018). In contrast, other studies have suggested that little or no synergistic action took place, illustrating the complexity of the subject and the limited data that is available (Dupain et al. 2007; Bielansky et al. 2011; Malleswara Rao et al. 2012). It should be noted that lipids are generally considered to be easier to co-process than biocrudes/bio-oils as they are completely miscible with the fossil feed and are easily cracked under reactor conditions.

Earlier work by Melero et al. (2010) showed that increased coking resulted after the addition of vegetable oils to a FCC feed. However, this study was carried out in a MAT reactor which does not provide a realistic simulation of reactions in an FCC. These researchers also observed an increase in the formation of aromatic compounds when the percentage vegetable oil was increased in the FCC feed. More recently, Bezergianni et al. (2018) suggested that increased aromatics and decreased sulfur levels could be expected. Thus, it is apparent that the type of lipids/vegetable oils and the saturation levels of the fatty acids will have an impact on the products formed as olefinic bonds are more reactive.

As mentioned earlier, it is likely that co-processing oils and fats in the FCC will be the least risky strategy, since the fluidized FCC is designed to increase the value of heavy fraction of the crude with the catalysts regenerated onsite. However, only limited information has been reported on any commercial scale work (Chevron 2017). One limitation has been the availability of large volumes of cheap, representative feedstocks as, although Petrobras was able to catalytically cracked soybean oil to produce gasoline with higher octane number and lower sulfur and nitrogen levels, the large scale of the FCC made co-processing only possible at low blending levels (Pinho et al. 2014).

2.6   KEY CHALLENGES AND OPPORTUNITIES FOR THE OLEOCHEMICAL PLATFORM

There are arguably limited technical opportunities to further optimise the production of oleochemical-based drop-in biofuel as the major challenge is the cost, availability and sustainability of the lipid/oleochemical feedstocks. While waste feedstocks such as used cooking oil, tall oil, etc., can overcome sustainability concerns they are only available in limited volumes. Although significantly greater volumes of feedstock can be derived from vegetable sources such as rapeseed, soy and palm oils, sustainability and food security issues are likely to continue. Although "sustainable feedstocks" such as algae and non-food crops such as jatropha, camelina, carinata, pennycress, etc., have been the subject of extensive research and development this area is still evolving.

A major challenge is that vegetable oil prices are often higher than diesel prices. For example, palm oil had an average commodity price of US$598/ tonne ($0.598/L) while at the same time diesel fuel had a price of $1.50 USD/gal ($0.396/L)[26]. The price of soybean oil for the same month was $738.5/tonne ($0.738/L). As the feedstock constitutes about 80% of the cost of HEFA production, sourcing of low-cost, "sustainable" feedstocks such as used cooking oil (UCO) or tallow has been a major focal point. However, due to limited supply and increased competition the price for UCO has increased. In the US UCO was $27-28/cwt or $540-560 per metric tonne in July 2017[27].

It is important to note that FAME biodiesel and HEFA renewable diesel compete for the same feedstock and that FAME biodiesel is much cheaper to produce. However, under current policies in the USA there is no distinction between these products. It is also worth noting that the IEA does not consider HEFA to be an advanced biofuel. Consequently, if this definition is used, policies promoting advanced biofuels will not necessarily incentivise HEFA production. In contrast, in the EU, biofuel produced from wastes such as UCO can be double counted to meet that jurisdiction's Renewable Energy Directive.

As mentioned earlier, waste oils (e.g., tall oils) and used cooking oils (UCO) have been used as feedstocks for drop-in biofuels. One benefit with these types of feedstocks is that, compared to purpose grown plant

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[26] [IndexMundi New York Harbor Ultra-Low Sulfur No 2 Diesel Spot Price, US$ per gallon As of: Monday, July 17, 2017 Source: US Energy Information Administration) Commodity Prices - Price Charts, Data, and News http://www.indexmundi.com

[27] [USDA (2017) https://www.ams.usda.gov/mnreports/lswagenergy.pdf

derived oils, the carbon footprint of these "used oils" has already been absorbed by the life cycle of another product or service. A recent report by Ecofys concluded that crude tall oil (CTO) could be considered as a residue with a low ILUC risk and thus suitable for biofuel production. However, crude tall oil production (30-50 kg per tonne of pulp) is limited to about 2.6 million tonnes worldwide (Peters and Stojcheva 2017) and this potential feedstock is already used in several applications. Therefore the cost and actual availability is not clear. Similarly, although algal derived lipids could serve as a feedstock for the oleochemical platform, the economics have proved challenging as is covered in more detail in the recently updated IEA Bioenergy Algal Biofuels Task 39 report[28].

In summary, the oleochemical/conventional route to drop-in biofuels production will continue to predominate for the short-to-mid term, primarily due to the low oxygen content and high H/C ratio of oleochemical feedstocks and the relative maturity of the technology. The oleochemical/conventional platform is already producing HEFAs at commercial scale with a total global capacity of about 5 BL per year. Although this represents a small fraction of total global transportation fuel demand, it provides the vast majority of commercial drop-in biofuel that has been produced and used to date.

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3. THE THERMOCHEMICAL PLATFORM

Thermochemical processes use high temperatures and catalysts to convert biomass to liquid biofuels and chemicals as well as heat and power (Brown, 2011). While oleochemical/conventional routes to drop-in biofuels will typically use lipid/oleochemical feedstocks, thermochemical/advanced routes to drop-in biofuels will use some form of biomass as the feedstock. In the thermochemical process biomass is reacted at high temperatures (> 500 °C) to form carbonaceous gases and liquids as well as char solids. The two main thermochemical routes to drop-in biofuels that have been pursued include gasification and liquefaction. The gasification process, as the name implies, converts biomass mainly to a gaseous intermediate, known as syngas. The liquefaction process, on the other hand, maximizes the production of liquids, also known as pyrolysis oils, bio-oils or biocrudes[29]. The gaseous and liquid intermediates of these thermochemical processes need to be further processed to produce drop-in fuels or blendstocks.

Using the Fischer-Tropsch catalytic process, syngas can be catalytically condensed to form liquid hydrocarbon mixtures known as FT liquids that, in turn, can be upgraded to fuels for gasoline, diesel and jet engines. Similarly, biocrudes can be upgraded to liquid transportation fuels after further processing using catalysts and hydrogen. The main objective of catalytic upgrading is to remove the oxygen from the bio-based intermediates to produce petroleum-like hydrocarbon fuels. Biocrude upgrading processes are usually conducted in relatively complex facilities that require both high hydrogen inputs and capital costs (Bridgwater, 2012). As noted earlier, in most thermochemical processes there is a trade-off between capital costs, product yield and the extent of hydrogen requirements.

3.1 INTRODUCTION

The thermochemical routes to drop-in biofuels require the production of feedstocks/intermediates via pyrolysis/HTL where the target product is liquid (bio-oil/biocrude) or via gasification where the target product is synthesis gases (syngas). By adjusting the processing conditions, pyrolysis maximizes the proportion of liquid products and gasification maximizes the proportion of gases. Typically, pyrolysis is conducted at intermediate temperatures of about 500°C, in the absence of oxygen. If fast pyrolysis is carried out, the residence time is reduced to a couple of seconds or less and the proportion of liquid yields can reach as high as about 75% by mass. In contrast, if gasification is optimised, the biomass is reacted

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[29] As the term bio-oil is often used to refer to lipids as well, the term biocrudes are preferred to prevent confusion.

under pressures of 1-40 bar, at temperatures exceeding 800 °C and in the presence of regulated amounts of oxygen. Under these conditions the production of gases is favoured and can reach up to 85% by mass of the total products (Bridgwater 2012). However, the product composition that is obtained is highly dependant on the process that is used, with fast/catalytic/slow pyrolysis or gasification, all resulting in a range of different products as partially summarised in Figure 9.
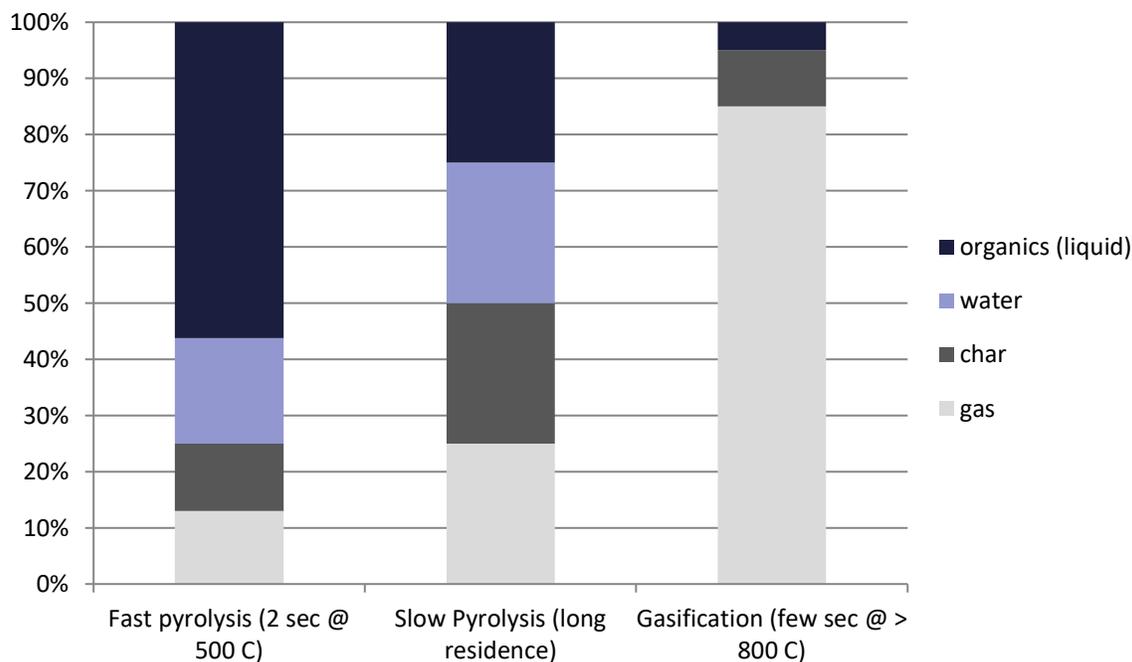
Figure 9 Product spectrum from thermochemical conversion of biomass. Source: Bridgwater 2012

Syngas and bio-oils/biocrudes are intermediates that can be directly used as combustion fuels for stationary power applications such as burners, boilers, furnaces and industrial kilns. However, for drop-in biofuel applications, these intermediates need to be catalytically upgraded to oxygen-free hydrocarbons. This upgrading can take various forms. For example, Fischer-Tropsch (FT) condensation from syngas can be used to produce paraffins while hydrotreatment of liquid intermediates can be used to produce hydrotreated pyrolysis oils (HPO). To maximize yields, both of these upgrading technologies use specialized catalysts and hydrogen inputs. The resulting FT liquids and HPOs are hydrocarbon mixtures that need to be distilled and potentially hydrocracked in order to produce the desired fuels which usually includes a mixture of gasoline, jet and diesel range hydrocarbons (Figure 10).
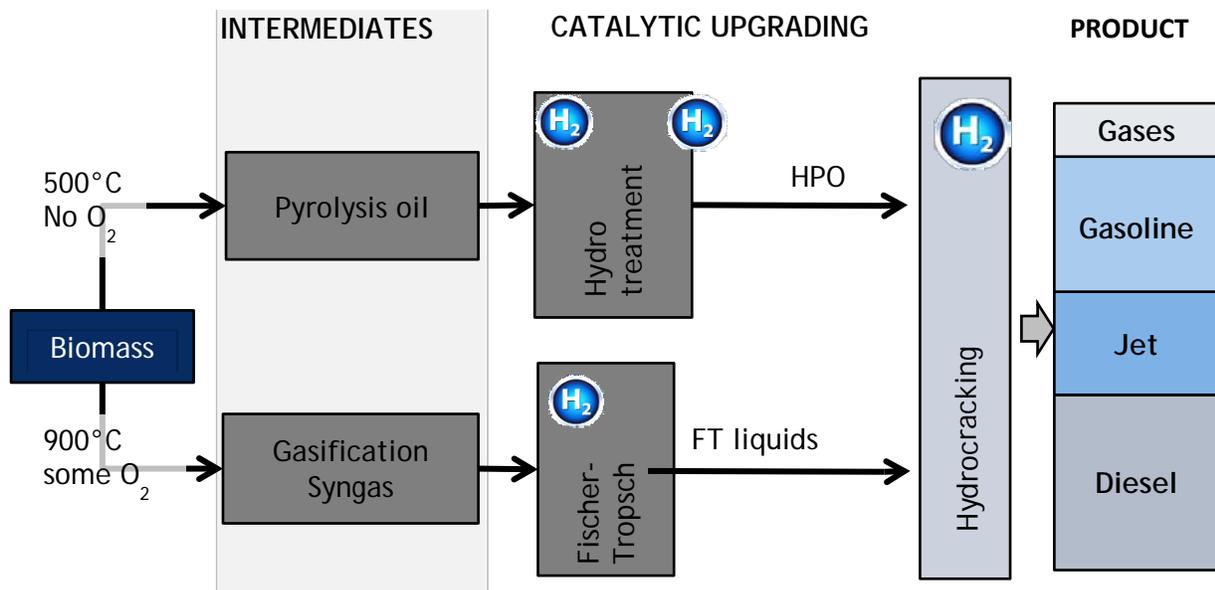
Figure 10 Simplified representation of major thermochemical drop-in biofuel process routes.

As has been discussed, although pyrolysis and gasification have many fundamental characteristics in common, the two processes differ markedly with respect to upgrading, drop-in fuel yields, capital costs and hydrogen (H_2) requirements.

3.2   THERMOCHEMICAL LIQUEFACTION

The three main types of thermochemical liquefaction technologies include fast (conventional) pyrolysis, catalytic pyrolysis and hydrothermal liquefaction (HTL).

One of the important differences between these technologies is the characteristics of the liquid product, particularly the amount of oxygen in the bio-oil/biocrude. Fast pyrolysis generally produces a bio-oil with high oxygen levels (>40%) while much lower levels of oxygen are achievable with catalytic pyrolysis and/or hydrothermal liquefaction (5-25%), depending on process conditions. From a technical upgrading perspective, the oxygen content is very important as it will impact the stability of the bio-oil and the extent of external hydrogen required, etc. (as detailed in Section 1.3). It should be noted that several other parameters such as yield, etc., will influence the broader feasibility and economics of each process.

3.2.1 Fast Pyrolysis

Fast pyrolysis is a thermal decomposition process that requires rapid heating of biomass to about 500°C and a subsequent rapid cooling of the resulting vapours to room temperature. Upon cooling, these vapours condense to form the liquid bio-oil product. It has been demonstrated that rapid heating and cooling is crucial to maximizing bio-oil liquid yields at the expense of char and gas production (Bridgwater 2012). To maximize bio-oil yields (to about 75% of starting biomass by mass) rapid heating to the target temperature must be achieved throughout each biomass particle (i.e., within about one second). These high heat transfer rates (up to 1000 °C/s) ensure maximum devolatilization (vaporization) of the biomass solids and, so far, have only been achieved by a select number of reactor designs (Bridgwater 2012) with particle size also impacting the effectiveness of heat transfer.

The main reactor designs that have been used for fast pyrolysis are the bubbling fluidized bed, the circulating fluidized bed and the ablative or rotating cone reactors.

The Bubbling Fluidized Bed (BFB) reactor is well suited for fast pyrolysis (and effective heat transfer) as it uses a hot sand fluidized bed to achieve high rates of heat transfer to the biomass particles. The reactor beds are fluidized using a compressed carrier gas which is fed through the bottom of the reactor at sufficiently high rates to "fluidize" the solids (sand and biomass) while transferring the gas-entrained char upwards. They have proven to be relatively robust systems that achieve high heat transfer rates and uniform bed temperatures (Ringer et al. 2006).

As depicted in the simplified schematic of a typical BFB fast pyrolysis process (Figure 11) biomass is first dried and ground to a particle size of about 3 mm to facilitate rapid particle heating and devolatilization. These particles subsequently enter the fluidized bed pyrolysis reactor where they are rapidly heated to a temperature of about 500°C. After about a 2 second residence time, the generated vapours are vented to a cyclone where they are separated from the entrained solid char particles. The recovered char can be sold as a value-added product (e.g. soil amendments and activated carbon) or used as fuel for the furnaces that generate and compress the hot recycle gas that feeds the main pyrolyser reactor. The clean vapours are then swiftly transferred to a quench cooler where they are condensed to form the bio-oil. The uncondensed fraction of the vapours along with the permanent gases is then transferred to a second condensation train such as a coalescing filter, scrubber or electrostatic precipitator (e.g. Nexterra) where additional bio-oil is recovered. The remaining flue gas is fed to the furnace that generates hot gas for the

main reactor. It has been shown that fast pyrolysis oils contain up to 75% of the mass and 65% of the energy that was contained in the original biomass feedstock (Bridgwater 2012).
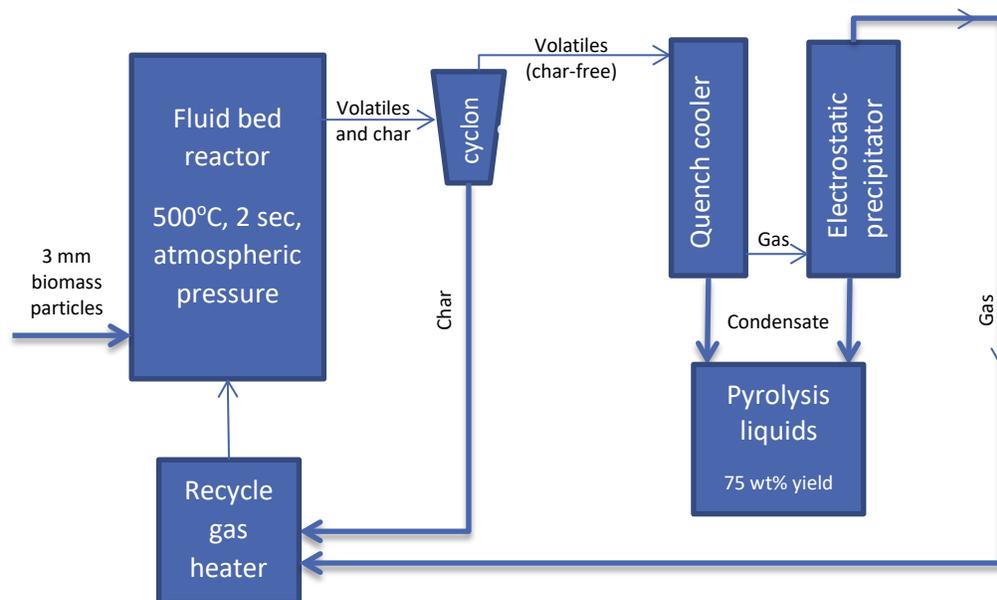
Figure 11 Simplified schematic of bubbling fluidized bed (BFB) fast pyrolysis. Source: adapted from Bridgwater, 2012

A more complex version of the bubbling fluidized bed (BFB) reactor is the circulating fluidized bed (CFB) reactor. This reactor configuration has been used by the petroleum industry for many decades within their fluidized catalytic cracking (FCC) units. This type of system (Figure 12) is similar to the BFB process other than the compressed recycle gas being fed at much higher velocities. As a result, the entire loose contents of the reactor (vapors, gases, char as well as the fluidized bed's sand particles) are carried into the downstream cyclone. The char and sand are then recovered from the cyclone and fed together to a combustor, where the char is burned off to heat up the sand. The cleaned hot sand (at about 800 °C) is then fed back to the main reactor entrained in the compressed carrier gas and the process cycle is repeated. Although this system is more expensive to install and operate than the BFB process, it comes with the advantages of constantly regenerating clean sand bed particles and achieving higher throughputs. It should be noted that the CFB process requires small, homogenous feedstock particles since the rapid gas flow only permits a very short residence time in the hot zone of the pyrolysis reactor. The CFB pyrolysis is the configuration of choice for the Canadian pyrolysis company "Ensyn" who markets their technology under the name RTP (Rapid Thermal Processing). Other developers of the CFB

configuration include CRES (catalytic pyrolysis, Greece), ENEL (Italy) using Ensyn technology (Ringer et al. 2006) and a VTT-led consortium in Finland (Metso, UPM, Fortum).
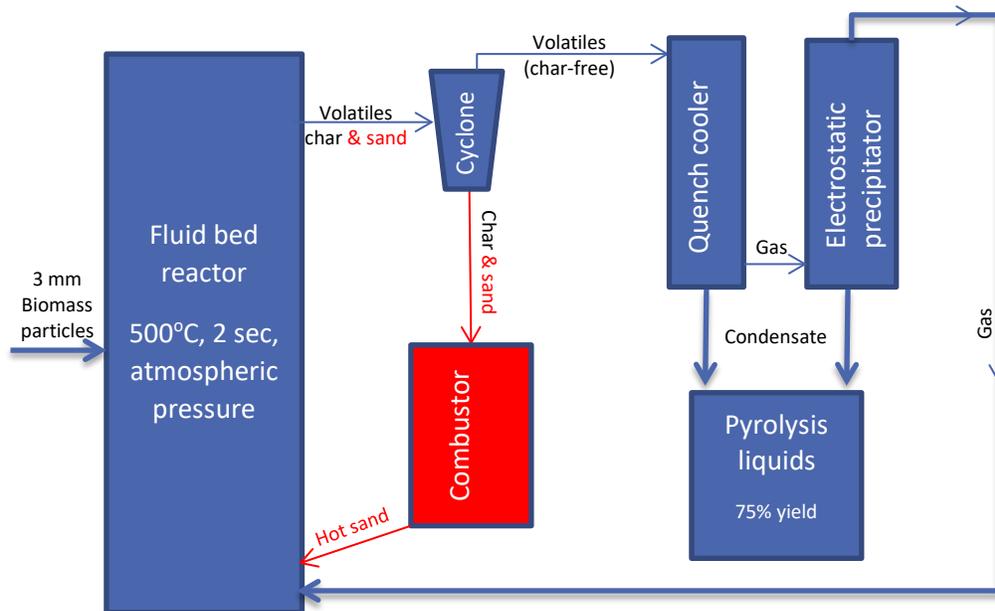
Figure 12 Simplified schematic of circulated fluid bed (CFB) fast pyrolysis. Source: adapted from Bridgwater, 2012

The main drawbacks of fluidized bed reactors are their reliance on a compressed carrier gas which often carries char contaminants to the bio-oil product. Gas compression also requires high capital and operating costs. As the carrier gas used to mix and circulate the sand bed carries char particles of such small submicron size that even the solids separation cyclone cannot capture them, these tiny particles remain entrained in the vapour that enters the quench cooler and they end up in the bio-oil product (Bridgwater 2012). This can be a problem as char particles can catalyze tar and coke formation and they can plug reactor pipes and filters upon subsequent bio-oil upgrading. The type of metals in the char particles also has an impact on tar formation, with alkali metals having the greatest impact. It should also be noted that the compressors used to deliver high speed carrier gases are capital-intensive and they are not well suited for small scale applications (Wright et al. 2010).

Alternative reactors that do not use a carrier gas have recently been developed. These reactors use centrifugal forces and mechanical motion to achieve the high rates of heat transfer needed to rapidly volatilize the biomass particles. These types of pyrolysis reactors include ablative and rotating cone designs based on the principle of sliding biomass particles against a hot surface, thus "melting" the fibre

in a similar way that a block of butter melts when pressed against a hot surface. Ablative pyrolysis reactors do not use a fluidized bed or sand particles while rotating cone reactors use sand particles contacting biomass particles, but without using fluidization by a carrier gas (Venderbosch and Prins 2011; Bridgwater 2012). The concept of ablative pyrolysis was first proposed by the CNRS laboratories in Nancy, France. Subsequent ablative reactor designs have been developed by NREL in the USA (vortex reactor) and by Aston University in the UK (plate reactor) (Bridgwater, 2012). The company Pytec has a demonstration plant for ablative pyrolysis in Germany. The rotating cones reactor concept was initially developed by the Dutch Company BTG (a University of Twente spin-off) who currently operate a 5 tonne biomass feed per hour facility in the Netherlands (Empyro BV) and who also supply bio-oil commercially through an online store[30]. BTG also designed and built a 48 tpd facility which operated in Malaysia several years ago (see Table 7 below). The Empyro project started construction in 2014 with the plant opening in Hengelo (The Netherlands) in 2015. The production capacity is designed to increase gradually to more than 20 million litres per year[31] with 15 million litres of bio-oil produced in June 2017[32]. The bio-oil was temporarily stored and transferred to a dairy producer, Campina, where it was used as a fuel for a steam boiler. The steam produced was used by neighboring AkzoNobel. Currently, the pyrolysis oil produced by Empyro is thought to be the only bio-oil that can be ordered online[33].

Another carrier-gas-free pyrolysis reactor is the "auger" or "screw" reactor which has been used for more than 50 years in coal degassing and heavy oil coking applications (Meier et al. 2013). Due to the relatively poor heat transfer through the auger shell, this technology cannot be classified as fast pyrolysis as it is only able to heat up the biomass relatively slowly. Auger reactors also produce lower amounts of bio-oil as their slower heating and longer residence time characteristics favour greater solids formation (a more "charcoal-like" process). However, it has been shown that the low-grade liquid and the char can be recombined after recovery to produce pyrolysis "slurries" which can serve as an improved feed for gasification. The energy density of the slurry can be in the range of 18-25 GJ/m^3 and is typically higher than char-free bio-oils (ca. 21 GJ/m^3) or raw biomass (Dahmen et al. 2012). An example of such a system is the Bioliq™ process from KIT in Germany which planned to use auger derived slurries to feed central

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[30] https://www.btg-btl.com/en/technology

[31] http://www.biofuelsdigest.com/bdigest/2014/05/27/empyro-breaks-ground-on-biomass-pyrolysis-oil-production-plant-in-the-netherlands/

[32] https://bioenergyinternational.com/biofuels-oils/empyro-passes-15-million-litre-milestone

[33] https://www.btg-btl.com/en/company/services/shop

large scale gasification facilities (Meier et al. 2013). If both char and bio-oil are desired as co-products, the auger reactor may be a viable approach.

Although several groups around the world are pursuing biomass pyrolysis, the current production capacity for fast pyrolysis oils is quite low. Bio-oil facilities that have been or will be operated at the semi-commercial scale (> 50 tpd) are listed in Table 7 together with their characteristics and reactor type. Most pyrolysis facilities to date are based on CFB and BFB reactor designs which, as mentioned earlier, are relatively robust, scalable and result in relatively high yields of bio-oil.

Ensyn, operates a commercial plant in Renfrew, Ontario producing three million gallon biocrude annually. This biocrude has been qualified by the US Environmental Protection Agency under the U.S. Renewable Fuel Standards (RFS2) program. Although the facility was originally commissioned in 2006 to produce specialty chemicals and heating fuels, it was converted to a dedicated biocrude production facility in 2014[34].

In 2016, the Cote Nord Project in Port-Cartier Quebec was announced. The Project will convert approximately 65,000 dry metric tons per year of forest residues from local sources to produce 10.5 million gallon biocrude. The Cote Nord Project is currently in startup mode (Q4 2018)[35]. The biocrude produced will be sold mainly for heating purposes and as an intermediate for co-processing in oil refineries.

The company is also pursuing two other projects in Georgia, USA and Brazil. All the projects were using the same RTP conversion process to produce biocrude, which has been engineered by Honeywell UOP through a contract with Envergent Technologies (a joint venture between Honeywell UOP and Ensyn)[36].

In parallel, some pyrolysis technology providers have focussed on small scale (1-5 tpd) and mobile pyrolizers. These units are described as mobile densification facilities that produce liquid bio-oils or bioslurries which are intended to be subsequently transported and processed or upgraded at large, centrally located facilities. These plants can also be co-located with oil refineries to take advantage of co-processing opportunities. Some of the companies pursuing mobile pyrolizer systems development include

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[34] http://www.ensyn.com/ontario.html
[35] http://www.ensyn.com/quebec.html
[36] http://www.ensyn.com/honeywell-uop.html

Canada's ABRI-Tech, California's Cool Planet and ROI in Alabama (Meier et al. 2013). Battelle's[37] ton-per-day pilot mobile pyrolizer in Ohio can convert pine chips, shavings and sawdust into up to 130 gallons of wet bio-oil per day[38].

Table 7 Commercial and pre-commercial (≥ 50 tpd) bio-oil facilities by 2017.

Company	Location	Status	Capacity (ODT)	Application	Reactor type
Fortum, Finland[39]	Joensuu CHP plant	Demonstration	303 tpd*	CHP fuel	CFB integrated with CHP system (Metso design)
Ensyn, Canada	Renfrew, Ontario	Commercial	70tpd(nameplate)	Bio-Oil[40]	CFB (Ensyn design)
	Quebec, Canada	In process of being Commissioned	200	Bio-oil	CFB (Ensyn design)
Kerry group/Red Arrow, Ireland/USA	Rhinelander,Wisconsin, USA		3x(30-40)tpd[41]	Food flavouring /browning products and CHP fuel	CFB (Ensyn design)
BTG-BtL Malaysia	Palm oil processing facility	Not operating	48 tpd	Cofiring with waste	Rotating Cone (BTG design)
	Hengelo, the Netherlands)[42]	Commercial	120 tpd (nameplate)	CHP fuel	Rotating Cone (BTG design)

*calculations based on 330 day/year operations. Sources: (Fortum 2013; Ensyn 2017; Oasmaa and Czernik 1999; BTG 2012)

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[37] http://www.biofuelsdigest.com/bdigest/2013/11/11/is-it-the-future-of-fuel-new-battelle-mobile-pyrolysis-unit-nets-130-gallons-of-bio-oil-per-ton/

[38] http://www.biofuelsdigest.com/bdigest/2015/08/03/the-pyromaniax-class-of-2015-the-top-10-pyrolysis-projects-in-renewable-fuels/

[39] https://www.cif-ifc.org/wp-content/uploads/2016/10/First-Commercial-Pyrolysis-Oil-Plant-_-DEMO-2016_-Sikanen.pdf

[40] http://www.biofuelsdigest.com/bdigest/2015/08/03/the-pyromaniax-class-of-2015-the-top-10-pyrolysis-projects-in-renewable-fuels/

[41] http://www.ensyn.com/licensed-production.html

[42] https://biorrefineria.blogspot.ca/2015/06/empyro-project-commercial-scale-fast-pyrolysis-plant.html

3.2.2 Catalytic pyrolysis & others

Catalytic pyrolysis is a process that combines pyrolysis with zeolite cracking in a single step (Butler et al. 2011). Catalytic pyrolysis is divided into *in situ* and *ex situ* pyrolysis processes. *Ex-situ* catalytic fast pyrolysis is an uncatalyzed fast pyrolysis integrated with a catalytic post-treatment of pyrolysis vapors before condensation (e.g. zeolite such as HZSM-5) to deoxygenate pyrolysis vapors and to produce aromatics and olefins. *Ex-situ* catalytic pyrolysis produces bio-oil with a lower oxygen content (ranging between 4 – 35%) and allows a lower temperature processing regime than conventional uncatalyzed fast pyrolysis. The advantage of *ex-situ* catalytic fast pyrolysis is that some of the polymerization and gum formation reactions are prevented that greatly reduce viscosity and instability of bio-oil (Pham et al. 2014).

In-situ catalytic fast pyrolysis is a process where the biomass is pyrolyzed at a lower temperature (i.e. less than 500°C) with loaded catalyst (i.e. transition metal or precious metal catalysts) in the heating medium (e.g. sand) or impregnated with the biomass prior to the pyrolysis. When Wang et al. (2014) compared *ex-situ* and *in-situ* catalytic pyrolysis using a micro-reactor system they found that *in-situ* pyrolysis produced more aromatics while *ex-situ* produced significantly more olefins. KiOR is an example of a company that employed *in-situ* catalytic pyrolysis with the technology based on a catalytic fast pyrolysis process using zeolite catalyst to convert the lignocellulose into bio-oil. The bio-oil could then be upgraded to transport fuel blendstock in a hydrotreater. However, the company filed for bankruptcy in 2014[43].

Another *in-situ* catalytic pyrolysis process (IH^2) has been developed by the Gas Technology Institute (GTI) in Des Plaines, Illinois in USA, 2009[44]. This process involves fast pyrolysis of the lignocellulosic biomass in a catalytic fluidized bed at around 350 – 460 °C under 20 – 35 bar of hydrogen (i.e. hydropyrolysis) with an average size of 900 – 1300 µm in size hydropyrolysis catalyst developed by CRI Catalyst, a project partner (Roberts et al. 2015). Although this process produces bio-oils with a low oxygen content (e.g. 4-10%,) in a single reaction step, scaling up and high hydrogen consumption remain as ongoing challenges.

Susteen Technologies GbmH is a spin-off company of the Fraunhofer Institute for Environmental, Safety, and Energy Technology UMSICHT. Susteen Technologies developed the innovative staged design thermo-catalytic reforming (TCR®) process for converting lignocellulosic biomass into high quality syngas, bio-oil,

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[43] https://www.independentsciencenews.org/environment/biofuel-or-biofraud-the-vast-taxpayer-cost-of-failed-cellulosic-and-algal-biofuels/
[44] https://ec.europa.eu/energy/sites/ener/files/documents/29_laxmi_narasimhan-ih2_advocacy_lead.pdf

biochar and water. The overall TCR process is described in the Susteen Technologies website[45]. Initially, the wet biomass feedstock is dried to between 70-90% dry matter content through a combination of standard mechanical and thermal drying technology. The TCR technology itself can supply sufficient heat for thermal drying of biomass with 60-70% water content. The biomass is then carbonized to biochar at intermediate temperatures (400-500°C) inside the first stage of thermo-catalytic reforming (TCR®) where the volatile organic compounds are extracted. In the second TCR reactor stage the biochar is heated up to 600-750 °C and again brought into contact with the volatile compounds. Through catalytic functions the organic compounds are cracked to quality fuel gases and oils. The steam reforming of water and carbon increases the yields of a hydrogen rich syngas. In the final step the liquid compounds are condensed and the product syngas cleaned in a relatively simple product treatment stage. One of the advantages of a staged process is that the TCR technology produces its own process energy through biochar combustion and on-site combined heat and power generation[45].

Annellotech, a spin-off company from Professor George Huber's group at the University of Massachusetts, is licensing a fluidized bed catalytic pyrolysis platform which produces a bio-oil rich in benzene rings (hence "Anello" Tech which in Latin means "ring"). The aromatic character of this biomass derived liquid means it is good feedstock for the subsequent production of BTX (Benzene, Toluene, Xylenes). The company is primarily focussed on these value-add chemicals[46]. In May 2017, Anellotech announced the successful continuous performance of the TCat-8 pilot plant as part of unit commissioning in Silsbee, Texas, converting loblolly pine into BTX and other valuable chemical by-products[47].

3.2.3 Hydrothermal liquefaction

Hydrothermal liquefaction (HTL) is another thermochemical liquefaction process which produces a biocrude intermediate that can be further upgraded into drop-in biofuels. Its main advance as compared to pyrolysis it that it can utilize wet biomass and results in a bio-oil/biocrude with a significantly lower oxygen content (5-18% oxygen), depending on the specific processing conditions (Elliott et al. 2015). The HTL process uses high pressures (e.g. 50 - 250 bar or more) and moderate temperatures (around 250-550 °C) as well as catalysts over 20-60 min to liquefy and deoxygenate biomass (Elliott 2007; Akhtar and Amin

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[45] http://www.susteen-tech.com/overview.html
[46] https://www.anellotech.com/about-us
[47] http://anellotech.com/press/anellotech-announces-first-successful-performance-test-its-tcat-8%C2%AE-pilot-plant

2011; Goudrian and Peferoen 1990). Process conditions range from subcritical to supercritical, depending on the technology and company.

It should be noted that the HTL process is not new and can be dated back as early as the 1920s (Jensen 2018). This was the foundation of later HTL technologies that attracted research interest, especially during the 1970s oil embargo. It was around that time that a high-pressure (hydrothermal) liquefaction process was developed at the Pittsburgh Energy Research Center (PERC) and demonstrated (at the 100kg/h scale) at the Albany Biomass Liquefaction Experimental Facility at Albany, Oregon, US (Elliot, 2007). At the same time Shell Oil developed the HTU™ process in the Netherlands. The HTU™ process applied pressures in the range 150-180 bar and temperatures in the range 300 to 350°C (Nielsen et al. 2012; Goudrian and Peferoen 1990). As an example, eucalyptus chips treated with HTU at 180°C and 180 bar for 6 min yielded 48.6 wt% DAF (dry and ash free basis) bio-oil, 32.8% gas and 18.6% aqueous phase. The oil contained 10% oxygen (Goudrian and Peferoen 1990). HTL oils can be very viscous and melting points of about 80°C have been reported (Elliott 2007).

Potential feedstocks for HTL include lignocellulosic biomass, organic waste, sludge, manures, peat, algae, as well as low-grade coals like lignite. While organic substances are insoluble in water under normal conditions, water can be a good solvent for non-polar substances under supercritical conditions (Tekin et al. 2014). An increase in the ionic product of water can minimize radical reactions (Jensen et al. 2017). The hydrothermal liquefaction of biomass usually occurs in the presence of an alkali metal and alkaline earth metal carbonate, bicarbonate or formate catalyst (e.g., Na_2CO_3).

As water is in a sub/super-critical state, the reaction involves both hydrolysis and/or degradation of macromolecules of biomass into small molecules. In this process, a substantial part of the oxygen in the biomass is removed by dehydration or decarboxylation. In comparison to fast pyrolysis, HTL has a lower oil yield but produces a relatively stable oil and does not require energy to dry the biomass feedstock.

Steeper Energy claims its so-called Hydrofaction™ technology can convert low-energy biomass feedstocks into a high energy density biocrude under super-critical condition, which can be further upgraded into finished fuels (Figure 13)[48].

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[48] https://www.bio.org/sites/default/files/0830AM-Perry%20Toms.pdf

HYDROFACTION™ TECHNOLOGY
TRANSFORMING LOW-ENERGY DENSITY FEEDSTOCKS INTO VALUABLE HIGH ENERGY LIQUID FUELS
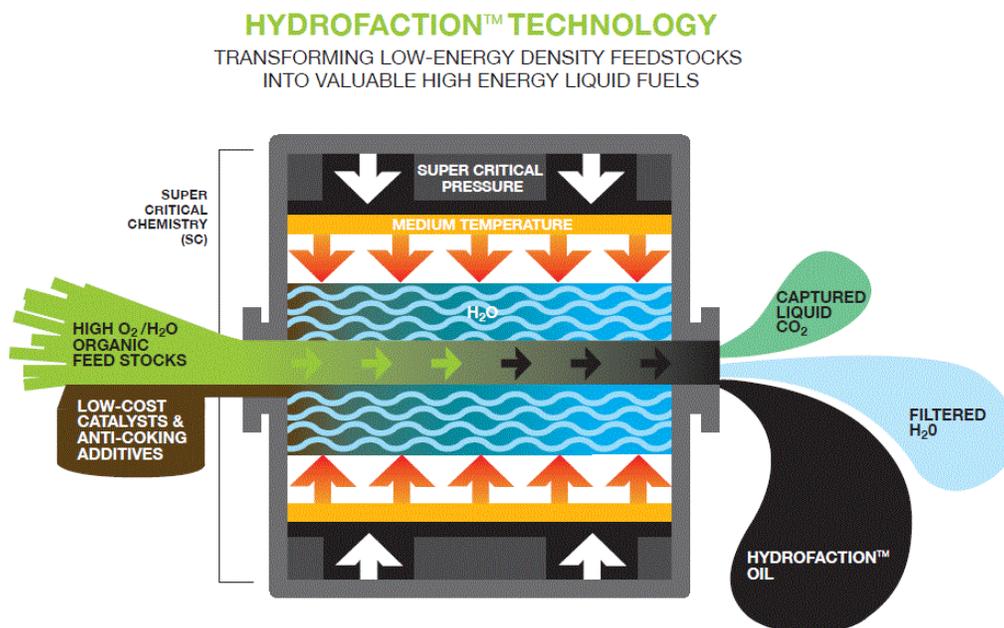
Figure 13 Illustration of the hydrothermal liquefaction (Hydrofaction®) technology developed by Steeper Energy Ltd[48].

In March 2015, Steeper Energy received a $3m grant from Sustainable Development Technology Canada (STDC) to develop an industrial scale pilot plant based on the Hydrofaction™ of biomass[49]. The goal of the project is to produce 100 barrels of biocrude per day (i.e. 4.35 MLPY). The industrial scale pilot plant will be co-located with the Daishowa Marubeni International (DMI) Alberta Peace River pulp mill. In December 2017, the company announced a partnership with Silva Green Fuel, a Norwegian-Swedish joint venture, to construct a $59 M demonstration plant at a former pulp in Tofte, Norway. Steeper has licensed its technology to Silva, who hope to build a 4,000 L/day facility over the next 18 months. Start-up is planned for spring 2019[50].

Licella, an Australian company, has been developing its catalytic hydrothermal reactor (CAT-HTR™) platform which uses subcritical water to convert biomass to bio-oil/biocrudes. The company has developed three pilot plants over the past 10 years (Table 8). In March 2016, Licella formed a joint venture with Canfor, a Canadian forest products company, with the goal of building a demonstration plant for the

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[49] http://www.biofuelsdigest.com/bdigest/2015/03/09/steeper-energy-receives-3m-grant-from-canadian-government/
[50] http://www.biofuelsdigest.com/bdigest/2018/01/16/the-silver-in-silva-the-story-of-steeper-energys-59m-advanced-biofuels-project-in-norway/

production of biocrudes from forest residues. A $13M non-repayable contribution from Sustainable Development Technology Canada will be used to further develop and demonstrate Licella's technology in Prince George, BC, where three of Canfor's pulp mils are located[51]. Feedstocks from Canfor's pulp mill in Prince George, British Columbia have been assessed at Licella's pilot plant in New South Wales, Australia. Canfor plans to integrate the Licella's technology into their pulp mills with final upgrading occurring at a local petroleum refinery. The project is estimated to cost $70 million.

Licella has also conducted trials on "end of life plastic" at their pilot plant in Australia and are currently pursuing two other joint ventures with Armstrong Chemicals in UK and iQRenew in Austrialia[52].

Table 8 Licella's Cat-HTR technology progress[53]

Plant	Construction	Capacity (slurry tonnes/annum)
1st Generation Small Pilot	2008	100
2nd Generation Large Pilot	2011	1,000
3rd Generation Large Pilot	2012	10,000

The Pacific Northwest National Laboratory (PNNL) has also been evaluating the potential of using both algae and wet sludge through as feedstocks that can be processed by their HTL process to produce biocrude with subsequent upgrading to transportation fuels. The PNNL HTL technology has been licensed to a Utah-based company Genifuel. Currently, Genifuel and Metro Vancouver hope to build a demonstration plan on Annacis Island, Greater Vancouver, British Columbia where the hydrothermal liquefaction facility will be used to treat wastewater[54].

3.3 BIO-OILS/BIOCRUDES – COMPOSITION, USES AND STANDARDS

Pyrolysis bio-oil (Py oil) is typically produced as a dark brown liquid composed of more than 300 different carbon molecules. Although referred to as an oil, with a similar physical appearance to crude oil, it is chemically distinct. It is suggested that the term biocrude is a more appropriate descriptor of lignocellulose-derived liquids/oils, as opposed to lipid-derived liquids/oils. In addition, differences in bio-oil characteristics and composition will always be apparent when using different process technologies and

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[51] http://www.biofuelsdigest.com/bdigest/2017/03/14/the-wonder-from-down-under-and-canadall-fund-er-canfor-picks-up-13m-for-licella-biofuels-project/
[52] http://www.licella.com.au/plastic/
[53] http://www.licella.com.au/facilities/
[54] https://www.labmanager.com/research-specific-labs/2017/06/pacific-northwest-national-lab-moves-forward-with-sewage-to-fuel-research#.XA7-znRKiCo

feedstocks. Generally, the term bio-oil mostly refers to fast pyrolysis bio-oils (FPO) as they have been more extensively characterised. Bio-oils or biocrudes from other processes are generally referred to more specifically such as catalytic pyrolysis bio-oils (CPO) or hydrothermal liquefaction biocrudes (HTL biocrudes).

Fast pyrolysis bio-oils (FPO) typically contain about 40% oxygen as compared to the typical maximum amount of 2% oxygen found in crude oil (Speight, 2006). As mentioned earlier, the relatively high oxygen content of biomass results in biofuels with undesirably high reactivity (low chemical stability) and low energy density. Compared to crude oil, bio-oil has less than 50% of its equivalent energy density (16-19MJ/kg vs 40 MJ/kg). Bio-oils/biocrudes derived from processes such as catalytic pyrolysis or HTL will typically have significantly lower oxygen content.

Most bio-oils have a smoky odour and their chemical composition is derived from the decomposition (depolymerisation and fragmentation reactions) of the main biomass components of lignin, cellulose and hemicellulose (Oasmaa and Czernik 1999). From a compositional perspective, bio-oils resemble woody biomass much more than they resembles crude oil. Consequently, in some ways, they can be thought of as "liquid woods". In fact, the terms "liquid wood" together with "bio-oil" are among the many alternative names that have been used in the literature to describe pyrolysis oils (Oasmaa and Czernik 1999). Due to this elemental resemblance to wood, bio-oil has the same effective H/C ratio of about 0.2 and would be placed at the same "step" as lignocellulosic biomass on the H/C "staircase" described earlier (Figure 4). This has implications for the hydrogen and processing needs of bio-oils when converting them to drop-in biofuels. However, the H/C ratio should be significantly higher for catalytic pyrolysis bio-oils or HTL biocrudes.

When the various properties of heavy fuel oil (HFO) (used in shipping) and FPO are compared (Table 9), the differences in the oxygen content, energy density, amount of dissolved water (up to 30%), and the poor distillation performance (1 vs 50% residue) are quite striking.

Table 9 Typical properties of wood pyrolysis bio-oil and of heavy fuel oil (HFO)

Physical property	Bio-oil	Heavy fuel oil
Water content, wt %	15-30	0.1
pH	2.5	-
Specific gravity	1.2	0.94
Elemental composition, wt. %		
C	54—58	85
H	5.5—7.0	11
O	35—40	1
N	0—0.2	0.3
Ash	0—0.2	0.1
HHV, MJ/kg	16-19	40
Viscosity (at 50°C) cP	40—100	180
Solids, wt %	0.2—1	1
Distillation residue, wt. %	up to 50	1

Source: (NSF 2011; Oasmaa and Czernik 1999)

The table below (Table 10) compares typical properties of biocrudes from lignocellulosic feedstocks to highlight the differences between the technologies.

Table 10 Comparison of typical properties of bio-crude from lignocelulosic feedstock via different technologies with crude oil

	Fast pyrolysis [1]	Catalytic fast pyrolysis [2]	Hydrothermal liquefaction[3]	Crude oil
Water, wt%	15-30	8.3	0.8	0.1
pH	2-3	2.6	~8	--
HHV, MJ/kg	16-19	30.4	38.6	44
$\mu_{50°C}$, Cp	40-100	285*	17,360***	180
C, wt%	55-65	72	81.4	83-86
O, wt%	28-40	21.5	9.8	<1
H, wt%	5-7	6.4	8.7	11-14
S, wt%	<0.05	--	0.01	<4
N, wt%	<0.4	0.02	0.095	<1
Yield, wt%	55-75	32(18**)	45.3	--
HDO's H_2, Scf/bbl fd [4]	~3400	--	~1800	358-1150

[1] Data taken from Mortensen et al. 2011; Dabros et al. 2018
[2] Data taken from Passikallio 2016; *measured at 40 ℃; **recovered in the bio-oil fraction
[3] Data taken from Jensen et al. 2017; ***measured at 40 ℃
[4] Hydrogen required consumption for hydrotreatment, scf/bb fd (standard cubic feet/barrel feed) (Holladay, 2014)

Water is a major component of bio-oils and its concentration varies depending on the initial moisture content of the biomass and the pyrolysis conditions used. Severe pyrolysis conditions (high temperature and residence time) typically results in the removal of more water but also promote vapor polymerizations, thus increasing the viscosity and solids content of the resulting bio-oil (Oasmaa and Czernik 1999). Water is derived from both the original water in the feedstock and from the water formed during the dehydration reactions occurring during pyrolysis. An excessive amount of water in bio-oils is undesirable because it acts as a heat sink during combustion and it can also promote destabilization and phase separation of the fuel during storage.

However, a certain amount of water in the bio-oil is desirable as it helps reduce viscosity. For example when VTT studied the influence of the water content on various softwood bio-oils they found that, when the water content dropped below 25%, the viscosity increases dramatically and an unacceptable degree of bio-oil destabilization occurred (Lehto et al. 2013).

As well as water, the other major chemical components of bio-oil include hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids and phenolics (Bridgwater 2012). As was the case with water, the amount of these compounds in the bio-oil depends on the composition of the original biomass as well as the pyrolysis conditions used. Some of these components, such as the sugars, are hydrophilic but others, such as the phenolics, are more hydrophobic. Consequently, most bio-oils can be considered to be micro-emulsions. The continuous phase of the emulsion is the aqueous solution, which contains the polysaccharide decomposition products, while the discontinuous phase predominantly contains pyrolytic lignin (the emulsion is mainly stabilized by weak hydrogen bonds). The breakdown of this emulsion results in the formation of two phases, a lighter, more aqueous phase and a heavier, less aqueous (Bridgewater, 2012).

The "aging" of pyrolysis oils is measured as increased viscosity over time and it occurs through reactions between the oxygenated carbon molecules in the bio-oil emulsion. Polymerization reactions between double bonded components as well as esterification and etherification reactions between hydroxyl and carbonyl groups produce high molecular weight, water-insoluble components such as gums. These reactions lead to increased viscosity and, ultimately, to a phase separation of the bio-oil into an upper aqueous phase (containing a higher proportion of acids and sugars) and a lower tar phase (containing less water and a higher proportion of water insoluble solids and lignins) (Lehto et al. 2013).

The main factors that accelerate these undesirable "aging" reactions are (Oasmaa and Czernik 1999):

- **Time**: most bio-oils destabilize/phase-separate after storage for about 6 months or more at room temperature.
- **Temperature**: very important!: For example the viscosity of a hardwood bio-oil doubled after a year at room temperature, after a week at 60 °C and after a day at 80 °C.
- **Alkali char**: catalyzes polymerization reactions thereby increasing bio-oil viscosity.

The stability of bio-oils can be improved by removing char particles using hot filtration (Sitzmann 2009) or by adding solvents (Lehto et al. 2013) to improve the stability of the emulsion. For example, methanol blending is a relatively inexpensive method that has been shown to greatly improve the stability of bio-oils when used as burner fuels (Diebold, 1999). In earlier work, Diebold & Czernik (1997) showed that a 10% methanol blending reduced the bio-oil aging rate 20-fold. Although these and other stabilization techniques have been discussed earlier (Diebold, 1999; Oasmaa & Czernik, 1999), nearly all of the options are costly and/or lead to bio-oil yield loss. The impact of added solvents on the life cycle assessment is also likely to be detrimental.

Due to the substantial amounts of non-volatile materials, such as sugars and oligomeric phenolics, etc., that are typically found in bio-oils, they are unsuitable for distillation. The slow heating of the oils during distillation accelerates the polymerization reactions resulting in the formation of heavy and non-volatile compounds. Heavy Fuel Oil typically leaves a residue of about 1% after vacuum distillation whereas a bio-oil leaves up to 50% of the starting material as distillation residue. This poor distillation performance has implications not only for further processing of bio-oils (e.g. to drop-in fuels) but also in their use as fuels for combined heat and power applications.

Bio-oils have primarily been used as fuels for burner/boilers/furnaces for stationary heat and power generation. In general, liquid fuels are easy to store, transport and combust and they can also be pumped and fed into a burner through a spraying atomizer, thus improving heat transfer through the fuel droplet and maximizing combustion efficiency (Lehto et al. 2013). However, as discussed earlier, bio-oils contain large amounts of water and oxygenated compounds as well as char particles. They also have drawbacks as combustion fuels including ignition difficulties, high viscosity and instability as well as low pH and high particulate levels. Although bio-oils generally produce less NOx and SOx than do fossil fuels (coal and oil), they typically emit more particulate emissions due to the char content of the bio-oil (Lehto et al. 2013).

Various trials have burned bio-oil in heat and power facilities (Czernik and Bridgwater 2004; Bridgwater 2012; Venderbosch and Prins 2011) demonstrating the need for modified bio-oil storage and feeding

systems. The company Red Arrow (acquired by the Kerry Group in 2015) has been operating five facilities (licensed by Ensyn) in Wisconsin with the three largest unites each processing 30-40 dry ton/day of wood residue. The bio-oil is used for food flavoring and for heating fuels[55]. Fortum's (Finland) bio-oil is used for district heating[56] with the plant commissioned in 2013 and a capacity of 100,000 dry tonnes of wood and 50,000 tonnes of bio-oil produced annually. Ensyn's facility in Ontario is capable of producing 3 million gallons/year of bio-oil with most of this oil sold for stationary heating to clients in the US[57].

One potential use of bio-oils is to co-fire them with conventional fuels such as coal, as was demonstrated when Red Arrow's pyrolysis oils were co-fired in the coal power station at Manitowoc Public Utilities in Wisconsin (USA) (Venderbosch and Prins 2011).

As large-scale internal combustion diesel engines and gas turbines are more efficient in generating electricity than are boilers that feed steam turbines it would likely be beneficial if bio-oils could be used in these engines in the same way as heavy fuel oil is used. However, the corrosiveness and char content of bio-oils currently limits their use in these facilities. Possible solutions to these drawbacks include the incorporation of a low-pressure fuel supply system that preheats and filters the bio-oil, a nozzle design that allows larger fuel flows and dual fuel operation, the redesign of the hot section and the use of stainless steel parts and compatible polymeric materials. However, it is likely that these modifications will be costly and there is still no guarantee that the engine will operate trouble-free when using a bio-oil fuel (Venderbosch and Prins 2011; Lehto et al. 2013).

Bio-oil can also be used as a fuel for gasification facilities. As gasification is more sensitive to scale than pyrolysis, bio-oil production could be used as a method of densification to allow the transport of biomass over longer distances while providing the gasification facility with a more suitable feedstock as opposed to a likely more variable solid feedstock. The advantage of using a liquid as opposed to solid feedstock in gasification is the same as in combustion, namely the faster heat transfer through the fuel (R. Swanson et al. 2010) plus, grinding of biomass to small particle size is a very energy-intensive and costly operation. However, for certain gasification reactors, such as the entrained flow reactor, small particle size is

essential. The concept of using pyrolysis oils or slurries as a gasification fuel in order to improve access to remote biomass stocks is reviewed in more detail later in the gasification section.

As mentioned earlier, the composition of bio-oils can vary significantly, depending on the composition of the feedstock as well as the pyrolysis conditions used. This influences the use of bio-oils and their upgrading to transportation fuels. For example, feedstocks with high extractives such as resinous pine wood produce bio-oils with a frothy top layer representing up to 10% of the product's mass. Grasses are also less attractive pyrolysis feedstocks as they have a low lignin and high alkali ash content, both of which lead to lower bio-oil yields (about 60% compared to 75% for wood (Bridgwater 2012)). Although there tends to be a perception that thermochemical biofuel processes are "feedstock agnostic", in practice, feedstock variation is one of the major factors that contribute to the heterogeneity of bio-oils and their storage stability characteristics.

To overcome the commercialization hurdles resulting from the heterogeneity of bio-oils, a set of standards has been established by ASTM. The ASTM D7544-12 fast pyrolysis oil burner fuel standard was approved in 2010 for Grade G and in 2012 for Grade D bio-oils. The only difference between grades D and G is the pyrolysis solids and inorganics (ash) content (Table 11). These standards qualify pyrolysis oils as burner fuels and they provide benchmark-type minimum requirements upon which applications and trading of bio-oils can be based.

Table 11 ASTM standards for pyrolysis oils

Property	Grade G	Grade D
Gross heat of combustion, MJ/kg, min	15	15
Pour point, °C, max	-9	-9
pH	Report	Report
Density at 20°C, kg/dm3	1.1-1.3	1.1-1.3
Kinematic viscosity at 40°C, mm^2/s, max	125	125
Water content, % mass, max	30	30
Pyrolysis solids content, % mass, max	2.5	0.25
Ash content, % mass, max	0.25	0.15
Sulfur content, % mass, max	0.05	0.05
Flash point, °C, min	45	45

Source: (Nummisalo 2012)

The European Committee for Standardization (EU-CEN) has developed their own standard for use of fast pyrolysis bio-oil in heating (CEN/TR17103:2017)[58]. The standard identifies the key properties of fast pyrolysis bio-oils and their importance to the fuel quality for use in stationary internal combustion engines. The US Department of Energy BETO Office has also supported a project, jointly led by NREL, PNNL and ORNL, to determine standard methods of testing of bio-oils[59].

3.4 POTENTIAL COST OF BIO-OIL

As mentioned earlier, bio-oil is still produced at a relatively small scale and only limited volumes of bio-oil are available commercially. BTG in the Netherlands sells bio-oil in their online store with prices ranging from 100 euro for 2.5 kg to 7,500 euro for 1000 kg[60]. Although a recent article in Biofuels Digest indicated that pyrolysis bio-oil prices are competitive with heating oil at ~USD2/gallon[61], limited information is publicly available. The little information that is available suggests that pyrolysis oils are at about USD10/GJ (NREL (Ringer et al. 2006), KIT (Karlsruhe Institute of Technology, (Henrich et al. 2009), Aston University (Bridgwater 2012)). Although various parameters and assumptions differed between these techno-economic studies, there seems to be general agreement that bio-oil, produced at full scale facilities (2000 tpd), would cost around $10/GJ. This is two times the assumed cost (energy basis) of the raw biomass

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[58] https://shop.bsigroup.com/ProductDetail/?pid=000000000030353763
[59] https://energy.gov/sites/prod/files/2017/05/f34/thermochem_ferrell_2.5.2.303.pdf
[60] https://www.btg-btl.com/shop/show_articles
[61] https://www.biofuelsdigest.com/bdigest/2017/06/08/biomass-pyrolysis-comes-of-age/

($82-83/odt or ca. $5/GJ) and just over half the cost of bunker fuel which was selling at about 751 USD/tonne or USD18/GJ[62]. Although these estimates are subject to uncertainties and sensitivities, they indicate that there is currently about 50% cost margin that can be used to upgrade bio-oils to match HFO quality.

Although the pyrolysis route can produce a low-cost liquid fuel, bio-oils have some disadvantages when compared to low-grade liquid petroleum fuels such as HFO, with most of the challenges related to the relatively high oxygen content of the bio-oils. As mentioned earlier, to produce "petroleum-like" drop-in biofuels the oxygen has to be removed. Technology providers such as UOP have claimed that, depending on the upgrading efficiency of pyrolysis oils and the price trends of petroleum, bio-oil could be competitive. A 2005 UOP study suggested that gasoline from bio-oil would be economically attractive if bio-oil is available at $18 per barrel ($0.11 per liter) and crude oil sells for more than $50 per barrel ($0.31 per liter) (Marker 2005). This study suggested that bio-oils would have to be produced at 63% the cost of petroleum crude on an equivalent energy basis (per GJ). This reinforces the previous point that bio-oil needs to be at least half the cost (per GJ) of crude oil in order for the pyrolysis platform to be economically competitive.

It should be noted that policies can overcome cost barriers. For example, US "renewable" heating oil is currently eligible under the US Renewable Fuel Standard to earn RINs under D5 or D7[63].

3.5 UPGRADING BIO-OILS/BIOCRUDES TO TRANSPORTATION FUELS

As has been reviewed, physical upgrading of bio-oil can take place through hot-vapour filtration, liquid filtration and centrifugation (Bridgewater, 2012). Hot vapour filtration can reduce the ash content of the oil to less than 0.01% and the alkali content to less than 10 ppm (Scahill et al. 1997) which is much lower than the values obtained in systems using cyclones alone. Although the filtered bio-oil has a lower char content the char is catalytically active and can potentially crack the vapours and reduce the bio-oil yields to 20%. The low char content is also supported by the reduction in the bio-oil viscosity and average molecular weight. When the combustion performance of the vapor-filtered bio-oil was assessed by NREL

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[62] As of October 3, 2018; http://www.bunkerindex.com/prices/bixfree.php?priceindex_id=4; http://www.bioenergyadvice.com/facts/bio-fuel-units-of-measurement-energy-values-and-conversion-factors/
[63] https://www.epa.gov/renewable-fuel-standard-program/approved-pathways-renewable-fuel

(Scahill et al. 1997), VTT and Aston University (Sitzmann et al., 2009) they found that hot vapour filtration needed a very long processing time.

This earlier work also showed that liquid filtration of bio-oil is very difficult when filtering very low diameter particles (around 5 μm). This is a result of the complex interactions between the char and viscous components believed to be lignin oligomers which rapidly clog the filter with a gel-like substance. Solvents or self-cleaning filters have been used to overcome this problem (Bridgewater, 2012). Although UOP has indicated the desire to reduce the solids in the oil to below 0.01 wt.% and that pressure filtration may require up to 8 bar (Traynor et al., 2012) they have also suggested that centrifugation or ionic exchange may be a better alternative to remove the char from the bio-oil. While centrifugation has been shown to reduce the char content of the bio-oil it also reduces yield as some of the bio-oil is disposed together with the char cake.

As discussed previously, bio-oils can be used in various stationary heat and power applications or they can be upgraded to drop-in transportation biofuels such as diesel, gasoline and jet fuel grade hydrocarbons. However, although the relatively high oxygen content of bio-oils can be tolerated for direct combustion in stationary power applications, it is a significant problem for automobile engines and jet engines.

Upgrading of bio-oils to transport fuels involves extensive deoxygenation with the major challenge being the deoxygenation of the bio-oil while maintaining high conversion yields and high hydrogen to carbon ratios in the finished fuel. As pyrolysis liquids are significantly more challenging to upgrade than are vegetable oils various upgrading techniques have been proposed with the top two contenders being hydrotreating and zeolite cracking (Solantausta 2011). Although both processes are catalytic and selectively promote hydrogenation reactions, hydrotreating uses large amounts of hydrogen to remove water from bio-oils in the form of H_2O molecules. In contrast, zeolite cracking uses no hydrogen but instead rejects oxygen in the form of CO_2, thus lowering the biofuel yield. Both approaches elevate the effective H/C ratio of bio-oils from about 0.2 to about 2 in order to fit the functional properties of hydrocarbon motor fuels. Virtually all the current bio-oil upgrading processes originated in the petroleum industry and use specialized catalysts to improve reaction selectivity. As is recommended throughout this report, as capital costs for upgrading bio-oils are high it would be synergistically beneficial if existing oil refinery equipment could be used to process these biomass derived liquids.

A novel electro-deoxygenation (EDOx) process is also being assessed[64] that utilizes a ceramic membrane to selectively transport oxygen to upgrade bio-oil. This process can be integrated with a pyrolyzer and use electricity, overcoming the difficulties of securing large amounts of hydrogen gas. Integrated tests at PNNL performed on a slip stream of bio-oil resulted in a reduction of carbonyl groups and the elimination of carbohydrates. Subsequent work has proposed partial EDOx that uses the reactor to deoxygenate the bio-oil to a more stable point followed by complete deoxygenation with hydrotreating. However, further research on catalysts coking as well as scale up is still needed to prove the viability of the technology.

3.5.1 Hydrotreating

As mentioned earlier, hydrotreatment is a hydrogen-intensive process that deoxygenates and upgrades bio-oils to drop-in- transportation fuels. However, higher levels of hydrogen are required to hydrotreat vegetable oils when compared to petroleum sources. Even more hydrogen is required to hydrotreat bio-oils because they contain about 40-50 wt% oxygen compared to the 10% typically found in vegetable oils. As shown earlier on the H/C staircase diagram, the VOs have an H/C_{eff} ratio of about 1.8 while the bio-oil is around 0.2 (the same as wood). Thus bio-oils require more hydrogen and processing effort to become functionally equivalent to petroleum diesel. Similarly to hydrotreating vegetable oils, the targeted chemical reaction during bio-oil hydrotreating is the rejection of oxygen in the form of H_2O. This hydrodeoxygenation (HDO) reaction of bio-oil is conceptually represented as:

$C_1H_{1.33}O_{0.43} + 0.77H_2 \rightarrow CH_2 + 0.43H_2O$ (Bridgwater, 2012)
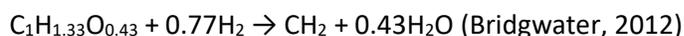
As described in the equation, the process uses about 1.5 (0.77 x 2) hydrogen atoms for every carbon atom produced in the final fuel. As the carbon conversion is 100% (as every carbon in the bio-oil is converted to a hydrocarbon) the resulting hydrocarbons should be of high quality since their H/C ratio is equal to 2. However, in practice, hydrotreatment is not so selective and the HDO reaction described above does not take place in isolation but rather in association with other reactions which divert carbon and/or hydrogen from the targeted liquid fuel product. These reactions include polymerization and condensation to form tars and coke, gasification reactions that form methane or CO_x and reactions that form low H/C hydrocarbons such as aromatics and olefins (Bridgwater, 2012). Thus, the low selectivity for

hydrodeoxygenation and hydrogenation reactions often leads to low fuel yields and high hydrogen requirements.

In most of the hydrotreating processes modelled so far the biomass to fuel yield is around 25% mass (55% energy) when hydrogen is provided externally and 15% (33%) when hydrogen is produced by gasifying the biomass (Brown 2011; Bridgwater, 2012). However, these relatively poor carbon yields and hydrogen use efficiencies can be improved through the development of more selective catalysts and optimized processes.

One of the future challenges facing increased hydrotreating of biocrudes is capacity. As discussed in the previous report, in the future, a doubling of US refinery hydrotreating capacity will likely be needed to meet the requirements for processing crude oils of deteriorating quality. A similar doubling or even tripling of today's US refinery hydrogen generation capacity would also be needed if the US refineries were to provide the hydrogen amounts needed to meet the US RFS cellulosic advanced biofuels mandate exclusively with pyrolysis-derived diesel. The US RFS has mandated 16 billion gallons per year of cellulosic advanced biofuels by 2022 (includes pyrolysis-derived diesel). If this entire mandate was to be met by biomass pyrolysis-derived fuels, around 267 facilities producing 60 million gallons per year (MGPY) of diesel/gasoline blendstocks would be required. According to techno-economic analysis by Jones at al. (2013) on biomass fast pyrolysis to automotive fuels, each of the 60 MGPY pyrolysis drop-in biofuel facilities would require a hydrogen generation capacity of 44 million standard cubic feet (SCF) per day. Assuming this hydrogen requirement would come from existing US refineries, a capacity of 11 billion SCF would be required by 2022. Current US refinery hydrogen generating capacity is about 3 billion SCF per day[65].

As described earlier, owing to the highly heterogeneous, oxygenated and reactive nature of bio-oils, their hydrotreatment is a lot more complex than that of petroleum. In oil refineries, hydrotreatment is mainly used to remove sulfur from petroleum feeds in a process known as hydrodesulfurization (HDS). The process conditions include temperatures that range between 300 and 600 °C, hydrogen pressures of 35 to 170 bar and liquid hourly space velocities (LHSV) of 0.2 to 10 per hour. The catalysts used in petroleum HDS are typically sulfided Co-Mo and Ni-Mo that are supported on porous alumina or aluminosilicate

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[65] https://www.eia.gov/dnav/pet/hist/LeafHandler.ashx?n=PET&s=8_NA_8PH_NUS_6&f=A

matrices. Unfortunately, for a number of reasons and as described below, these conditions are not suitable for processing bio-oils. These include:

- Sulfided Co-Mo and Ni-Mo catalysts, when in contact with bio-oils, are rapidly stripped of their sulfur and require constant resulfurization (addition of H_2S) to prevent catalyst deactivation (Huber, 2007). This deprives bio-oils of their low sulfur content advantage (Wang et al., 2013).
- Alumina supports create an acidic environment and they are not stable in the presence of water (irreversible dealumination) (Mortensen et al. 2011).
- Bio-oils are unstable at high temperatures as they can rapidly become viscous and eventually phase separate.
- Bio-oils tend to form coke residues, particularly in acidic environments and at high temperature and pressure. Coke is undesirable as it deactivates the catalysts by depositing on their active sites and it can severely plug reactor components (Wang et al., 2013).
- The water in bio-oil inhibits hydrotreating by modifying and deactivating the catalysts and by adsorbing onto active sites (Furimsky and Massoth 1999). Aside from the water content of bio-oils (up to 30%), more water is produced upon hydrotreatment.

These and other limitations have motivated the search for hydrotreating processes and catalysts that are better suited to the highly oxygenated and heterogeneous nature of bio-oils. Early research focused on adjusting process conditions and working with model bio-oil mixtures while using the same sulfided catalysts that oil refineries use for desulfurization (Huber et al. 2007). Although these alumina supported Co-Mo and Ni-Mo catalysts have various problems in processing bio-oils, they improve hydrotreating selectivity and they are widely available at a relatively low cost.

As mentioned previously, bio-oils are thermally unstable and they have to first be pretreated at lower temperatures in order to form a stable oil intermediate that can then be further hydrotreated at high temperatures. Although single stage hydrotreating of bio-oil at high temperatures has been attempted, it resulted in a heavy, tar like product (de Miguel Mercader et al., 2010; Jones et al., 2009) due to the polymerization, charring and eventually coking reactions which, at high temperatures, take place faster than the desired hydrotreating reactions. However, to achieve effective hydrotreatment high temperatures and hydrogen pressures at extended reaction times (up to 4 hours) (Elliott 2007) are often required. To fulfill these disparate condition requirements for stabilization and complete hydrotreatment

of bio-oils, a two-stage bio-oil upgrading approach is commonly used (Elliott, 2007; Jones et al. 2009). The first, mild, catalysed hydrotreatment stabilizes the bio-oil while a second, higher severity hydrotreatment stage, deoxygenates the fuel to transport-grade liquids. The first hydrotreatment typically forms at least two phases, one hydrophobic and one hydrophilic and effectively separates out a large proportion of the water within the bio-oil. The resulting hydrophobic liquid is more stable and amenable to further catalytic upgrading.

Earlier workers (Centeno et al. 1995; Ferrari et al. 2001) investigated the fundamentals of bio-oil hydrotreatment using traditional sulfide molybdenum catalysts on model bio-oil compounds such as ketones, esters and phenolics (while alcohols and carboxylic acids where formed in the process). They concluded that ketones react first at lower temperatures (> 200 °C) to form alkenes while carboxylic and phenolic groups were converted at higher temperatures (> 300 °C). This early work lead to a proposed reactivity scale for the major components of bio-oils (Figure 14) and the reactivity scale has proven to be a very useful rule of thumb in the absence of precise reaction kinetics. The olefins and other double bond species are the most reactive and can be hydrogenated to more stable components such as alcohols and alkanes at temperatures around 250 °C and below. Alcohols are dehydrated to olefins at temperatures closer to 300 °C while carboxylic groups are more recalcitrant than alcohols. Aromatics are the most recalcitrant and will only react at temperatures in the vicinity of 400 °C.
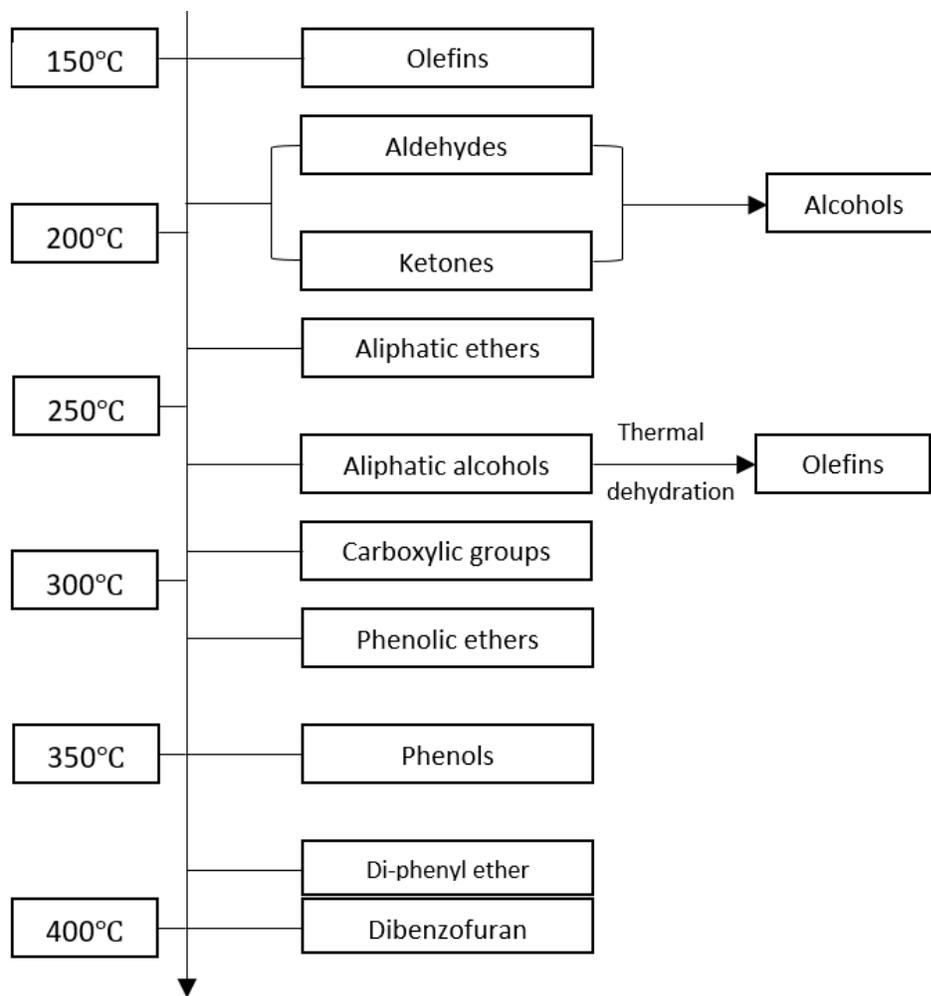
Figure 14 Reactivity scale of oxygenated compounds under hydrotreatment conditions.

Source: copied from Wang et al., 2013, based on work from Delmon and co-workers (Centeno et al. 1995; Ferrari et al. 2001) as adapted and plotted by Elliott, 2007.

As noted earlier, coking is a major problem during hydrotreatment as it can lead to catalyst deactivation and reactor plugging. In general, the parameters that promote coking are high temperatures, low hydrogen pressures, high acidity, and the presence of low H/C components such as phenolics, alkenes and highly oxygenated carbon molecules (Huber, 2007; Mortensen, 2011). Double bond molecules such as olefins, ketones and aldehydes are particularly prone to polymerization and coking. Fortunately, these species can be hydrogenated relatively easily during the first, low severity, hydrotreatment stage. This improves the thermal stability of the resulting bio-oil before the second hydrotreatment step. Refinery HDS catalysts promote the formation of coke by creating an acidic environment and promoting the

formation of aromatics. Aromatics are desirable up to certain concentrations since they form part of transport fuel blends, particularly gasoline (40% aromatics) (Bauen, 2009). However, aromatics are a low H/C ratio species and can act as precursors for coking reactions upon upgrading. The hydrogenation of aromatic rings is the most challenging as it requires high temperatures and hydrogen pressures (around 4.0 to 8.0 MPa of H_2) as well as highly active catalysts such as precious metals (Wang et al. 2013). Another way by which hydrogen can reduce coke formation is by converting catalyst-absorbed reactive species, such as alkenes, to stable molecules such as alkanes. In general the presence of hydrogen appears to play a pivotal role in minimizing the formation of coke.

While this more fundamental work has built an invaluable body of knowledge around the hydrotreatment and coking mechanisms of bio-oils, these studies have been mainly based on "model" as opposed to "real" bio-oils (Butler et al. 2011). In contrast, Elliott and co-workers (Elliott 2007) used sulfide Co-Mo and Ni-Mo catalysts on real bio-oil substrates and developed a two stage process that brings the oxygen content of the bio-oil down to < 1 wt%. The first stage of the process was conducted at 270 °C and 136 bar and the second at 400 °C and 136 bar. Consistent with the known challenges of these catalysts, the authors reported catalyst deactivation and formation of gums as major drawbacks of the process.

More recent research has focused on developing catalysts to circumvent the challenges encountered when using traditional HDS catalysts such as CoMo and NiMo supported on alumina materials. When precious metals such as Ruthenium, Palladium and Platinum were assessed as bio-oil hydrotreatment catalysts (Bridgwater, 2012) they performed better than CoMo and NiMo catalysts in terms of both hydrocarbon yields and H/C ratio of final product (Lin et al. 2011; J. Wildschut et al. 2009; Wang et al. 2013). They also proved to be more stable, less acidic and did not promote coking particularly when supported on non-acidic carbon. The company, UOP, has been a leader in using precious metal catalysts for hydrotreatment of petroleum. Together with PNNL they have assessed the potential of non-sulfided metal catalysts such as Ruthenium on bio-oils. Ruthenium seems to be the lowest cost and most promising of the precious metal catalysts assessed so far (Wildschut et al. 2010; Wildschut et al. 2009). When Lin et al. (2011) assessed various precious metal catalysts using the model compound guaiacol, they reported that the Rh-based catalyst showed the best HDO activity and a preference towards saturate benzene rings. Although precious metal catalysts are more favoured for bio-oil hydroprocessing, as they are more active in comparison to NiMo and CoMo based catalysts, their cost is so prohibitive that their use in industrial applications will likely be very limited.

The ability to recycle and the stability of Ru/C catalysts has been challenged by Wildschut (2009). When he conducted three successive hydrotreatment reactions (200 bar, 350 °C and 4.3 h each) where the catalyst was reused after repeated acetone washes, he found that the activity of the catalyst deteriorated even after the first repeat. After 2 repeats the oil yields dropped significantly (55 to 30%-wt.), whereas the amount of gas phase (5 to 11%-wt.) and solids (3 to 20%-wt.) increased, all indicating significant catalyst deactivation. This deactivation mostly affected the ability of the process to hydrogenate while it did not affect much of its ability to deoxygenate. The deactivation was attributed to sintering and coke formation on the surface of the catalyst.

The prohibitive price of precious metals means that novel catalysts have to be designed which will achieve high hydrotreating activity at lower cost. Although phosphide catalysts have been suggested as alternatives to sulfide catalysts they face similar issues. Once in contact with water they form phosphates which can deactivate the active sites on the catalyst (Wang et al. 2013).

Other than deoxygenation, the hydrogen treatment of bio-oils has many favourable side effects such as decreasing its water content, increasing its energy density (from 18 MJ/kg in crude bio-oil to 40 MJ/kg in hydrotreated bio-oil), decreasing its bulk density (from >1 in bio-oils to <0.8 in deoxygenated bio-oils), decreasing the coking propensity and decreasing its viscosity (from > 100cps in raw bio-oil to <5 cps in bio-oil that contains <5% oxygen) (Elliott 2007). All of these advantages result in higher yields and the higher H/C_{eff} ratio of the final transport fuel product. These benefits are generally absent in any bio-oil upgrading technologies that do not entail any hydrogen inputs.

3.5.2 Zeolite cracking

Zeolite cracking is a process used in the Fluid Catalytic Crackers (FCCs) of oil refineries and it has potential in bio-oil upgrading as a non-hydrogen consuming, non-pressurized alternative to hydrotreatment. The main deoxygenation mechanism of zeolite catalytic cracking is the rejection of oxygen in the form of coke and CO_2. The conceptual reaction of this mechanism is summarised below:

$$C_1H_{1.33}O_{0.43} + 0.26O_2 \rightarrow 0.65CH_{1.2} + 0.34CO_2 + 0.27 H_2O$$

When this formula is compared with the earlier equivalent formula for hydrotreating it is apparent that, in the absence of hydrogen, as occurs in zeolite cracking, bio-oil upgrading is poor. The theoretical carbon yields for zeolite cracking are low (65% compared to 100% in hydrotreatment) and the hydrocarbons produced have a low H/C ratio (1.2 compared to 2 for hydrotreatment). This low H/C ratio indicates that

the bio-oil is rich in aromatics and olefins and that the resulting fuel will have a low heating value, typically about 20-25% lower than crude oil (Balat et al. 2009; Mortensen et al. 2011). Similar to what occurs in hydrotreatment, the cracking reaction takes place alongside other undesirable reactions such as polymerization and coking which results in the diversion of some of the carbon from the targeted liquid biofuel. Thus, even in the presence of catalysts, cracking typically results in bio-oil-to-fuel yields in the range of 14-23 wt% of bio-oil (Balat et al. 2009), which is much lower than the theoretical 45 wt% yield which can be calculated from the equation above. This is largely because 26-39 wt% of the starting bio-oil goes towards the formation of solid tar and cokes (Balat et al. 2009).

Zeolites such as ZSM-5 and HZSM-5 are made of a highly porous aluminosilicate matrix and, as a result, they are typically not stable in the presence of bio-oils at high temperatures and pressures. Zeolite catalysts such as ZSM-5 have a strong acidity, high activities and shape selectivities which work well for upgrading petroleum feeds. However, for bio-oils, zeolite cracking poses severe catalyst coking and deactivation issues.

On the more positive side zeolite cracking requires no hydrogen gas and can operate at atmospheric pressures. This means that FCC-type systems can be used for bio-oil processing where the heavily coked catalyst can be rapidly regenerated in the FCC combustor. These systems have great potential to utilise the coke formed on catalysts as a fuel for heat and power generation. However, these systems often convert more biomass carbon to thermal energy than to liquid fuel products. Operating costs of FCCs are higher than regular fixed bed reactors because the faster recycling of carrier gas needed to regenerate the rapidly coked catalyst is highly energy intensive.

Other workers have (Vispute et al. 2010) proposed an approach that involves a mild hydrotreating step prior to zeolite cracking. The advantage of this approach is that it converts the most reactive oxygenated compounds, the carbonyls, to more thermally stable alcohols. In zeolite cracking carbonyl functionalities go directly to coke formation whereas alcohols contribute to the formation of valuable molecules such as olefins and aromatics. The introduction of a mild hydrotreatment step prior to zeolite cracking appears to result in bio-oil conversion yields (aromatics) as much as three times higher than direct zeolite cracking. This is particularly desirable for BTX (benzene, toluene, xylene) production which is the target of the Huber group's spin off company AnelloTech. However, the alkane yields are low and, while this technology may be relevant to making aromatic fractions for gasoline, it is not directly applicable to the production of the longer chain hydrocarbons that are needed for the production of diesel and jet fuels.

Cracking of bio-oils has also been attempted using platinum catalysts. Fisk et al. (2009) achieved a low oxygen bio-oil (2.8%) which was predominantly composed of aromatic and very few non-aromatic oxygenates. The oil yields of the process were rather low (10-20% wt of bio-oil was converted to stable oil) when compared to hydrotreatment upgrading (ca. 40%) (Fisk et al. 2009; Butler et al. 2011).

3.6   TECHNO-ECONOMICS AND SENSITIVITIES OF UPGRADING BIO-OILS INTO DROP-IN BIOFUELS

To produce drop-in biofuels bio-oils/biocrudes have to be upgraded and the commercialisation of the upgrading process is still evolving. Some estimates of the overall costs have been summarised by groups at Iowa State University (ISU), Pacific Northwest National Laboratory (PNNL), Idaho National Laboratory (INL) and National Renewable Energy Laboratory (NREL). However, direct comparisons between techno-economic analyses are often problematic. When Brown (2015) compared techno-economic assessments of different thermochemical pathways (Table 12) including fast pyrolysis followed by hydroprocessing (FPH) and catalytic pyrolysis with hydroprocessing (CPH), substantial differences were apparent. The three other studies (Jones et al. 2013; Li et al. 2015; Li et al. 2016) that were added were based on 2011 costs. Although a 2000 metric ton per day capacity was assumed, to try to decrease any variations, significant differences were still apparent. The Lang factor (the ratio of TPI to total purchased equipment cost) (Brown, 2015) varied from the most optimistic (3.73) to the most conservative (5.46) while plant life was assumed to be either 20 or 30 years in the different cases, which also affects the MFSP.

Table 12 Comparison of techno-economic analyses.

	Pathways	Capacity (MTPD)	TPI ($MM)	MFSP ($/gge)	MFSP ($/Lge)	Lang factor	Feedstock cost ($/MT)	Biorefinery life (years)
Jones et al. 2009	FPH	2000	329	2.21	0.58	3.73	60.5	20
Wright et al. 2010	FPH	2000	217	2.29	0.6	5.46	90	20
Jones et al. 2013	FPH	2000	700	3.39	0.89	4.4	80	30
Zhang et al. 2013	FPH	2000	379	3.04	0.8	5.46	86.52	20
Brown et al. 2013	FPH	2000	429	2.57	0.68	5.46	83	20
Thilakaratne et al. 2014	CPH	2000	457	3.69	0.97	5.1	96.57	30
Li et al. 2015	CPH, ex-situ	2000	638.5	4.27	1.13	4.08	80	30
	CPH, in-situ	2000	568.3	4.2	1.11	3.94	80	30
Li et al. 2016	FPH, SH[1]	2000	432.5	2.85	0.75	5.1	83[2]	30
	FPH, SHA[3]	2000	454.5	2.77	0.73	5.1	83[2]	30
	FPH, IH[4]	2000	-	2.33	0.61	5.1	83[2]	30
	FPH, IHA[5]	2000	-	2.25	0.59	5.1	83[2]	30

Based on 2011; 1: Standalone hydrocarbon; 2: Not including drying and grinding costs; 3: standalone hydrocarbon with alcohol as a byproduct; 4: integrated hydrocarbons; 5: integrated hydrocarbons with alcohol as a byproduct

An earlier US DoE Pacific Northwest National Laboratory (PNNL) (Jones et al. 2009) study was based on poplar bio-oil upgraded with a 2-stage hydrotreatment system using a conventional CoMo HDS catalyst. This work, which is still one of the most detailed publicly available studies to date, estimated a minimum fuel selling price (MFSP) of $2.04/gal ($0.54/L) with this price dropping to $1.74/gal ($0.46/L) when hydrogen is imported to the facility rather than produced on site from biomass. Importing hydrogen (made from natural gas) was considered more favourable in the near term since the conversion of biomass to hydrogen is currently inefficient and costly. There are also considerable capital cost savings achieved when hydrogen is imported as opposed to making it from biomass as the $303 million total project

investment (TPI) drops to $188 million when hydrogen is imported from an external source. For example, the TPI breakdown indicted how, out of a total cost of $303 million for the entire plant, only $92 million was the cost of the fast pyrolysis process components. The remaining costs were mostly related to the hydroprocessing infrastructure. Thus very substantial capital costs can be saved if the upgrading operations can make use of the hydroprocessing and hydrogen generation facilities available at an existing oil refinery. The PNNL study takes a somewhat more conservative (and appropriate) approach and uses the refinery only as a source of low cost hydrogen and as a possible facility to perform the final hydrocracking of the heavier portions of the highly deoxygenated (2% O_2) HDO. This approach resulted in a capital savings of $115 million.

However, some of the assumptions used in the 2009 PNNL study, such as feedstock costs of $51/t for a 2000 tpd facility, will likely need to be modified as recent studies have suggested that costs of around $80/t are more likely considering the logistic challenges and the competing end uses for biomass. The PNNL sensitivity analysis indicated that an $80/t feedstock cost would add about $0.20/gal ($0.05/L) to the MFSP. Assumptions that the hydrotreating catalyst will last at least 1 year is another sticking point. Although this is about the average life expectancy of catalysts used in refineries that hydrodesulfurize traditional petroleum cuts, catalysts that have been used to process bio-oils have so far proven to have much shorter life expectancies, primarily due to extensive coking. For example, PNNL's sensitivity indicated that halving the catalyst lifespan to 6 months added $0.15/gal ($0.04/L) to the base MFSP (minimum fuel selling price). However, Battelle, with the help of PNNL and Marathon Petroleum Corp., were able to meet the US Department of Energy's challenge of at least 1,000 hours of bio-oil hydrotreatment on a single catalyst charge [66]. They demonstrated more than 1200 hours on the hydrotreatment catalyst, using the previous described mobile pyrolizer. A recent PNNL's report (Jones et al. 2016), indicated improved catalyst lifespan by first using a sulfur guard, followed by deep stabilization and hydrodeoxygenation. In this way the catalyst life could be extend to 100 days while the guard bed (inexpensive base metal) lasted up to 60 days. In a US Department of Energy project peer review, March 2017[67], the group reported the removal of the sulfur guard bed which further increased the pressure of the stabilizer bed while catalyst regeneration extended the lifetime of the Ru catalyst. It was also reported

that the use of a carbide catalyst (Ni-Mo$_2$C), which consumes less H$_2$ as well as yielding a more stable conversion product comparing to Ru/C, lasted for 240 hrs before bed plugging due to fouling.

All of these studies have indicated that the MFSP (Minimum Fuel Selling Price) is very sensitive to feedstock cost, product yield and catalyst life and cost (Brown, 2015). Other workers have used uncertainty analysis (Li et al. 2015) to better indicate the minimum and maximum change of MFSP. In this work, the change in the feedstock cost resulted in a greater impact on MSFP than did IRR or TPI. However, it was with a narrow range within the 0.25/0.75 quartile, implying that financial assumptions may have more influence than the feedstock cost on MFSP.

As for capital costs, hydroprocessing and power generation equipment are the highest expenses and they must be weighed against the potential benefits of integrating the facility with a refinery and selling electricity to the grid. The 2010 ISU study also contrasted the capital cost of a first of kind plant with an nth plant facility. A pioneer plant would cost \$911 million (\$585 million for purchased Hydrogen) compared to a mature plant of \$287 m (\$200 m for purchased hydrogen scenario). This highlighted the high equipment risk involved in pioneer pyrolysis facilities, especially those that will produce hydrogen on site.

The three earlier techno-economic studies (Jones et al. 2009, Wright et al. 2010, Brown et al. 2013) generally agree on various points including that the cost of producing pyrolysis diesel would be in the vicinity of \$2.5/gal (\$0.66/L) which is equivalent to about \$19/GJ. This value (\$18/GJ) is similar to the earlier one calculated by the BIOCOUP group and indicates that upgrading to drop-in biofuels adds about \$10/GJ to the \$10/GJ base cost of making bio-oil. However, the study by Jones et al. (2013) described a significantly higher cost of producing drop-in biofuels from a fast pyrolysis platform. They showed the capital costs reaching \$700 million and the production costs as MFSP climbing to \$3.39/gal (\$0.90/L) or ca. \$26/GJ. Thilakaratne et al. (2014), Li et al. (2015) gave an even higher MFSP.

More recently researchers from Iowa State University have developed a novel bio-oil fractionation system that can condense bio-oil in five different stage fractions. When Li et al. (2016) simulated the production of biofuels using this system, several of the scenarios lowered the MFSP to less than \$3/gal. In addition, the models suggested that integration of this system with existing refineries could further bring down the MFSP to \$2.33/gal.

Again, these are rough comparisons based on different assumptions and are only meant to give a "high level" sense of the current estimated costs of pyrolysis derived drop-in biofuels. However, they can help

better identify the challenges and opportunities for cost reduction and eventual commercialization of pyrolysis-based drop-in biofuels.

3.7   REFINERY INTEGRATION OF PYROLYSIS PLATFORMS

As mentioned earlier, the majority of the processes and catalysts that have been used to upgrade pyrolysis oils originated in the oil refining industry. It has also been suggested that pyrolysis oils or their derivatives could be "dropped into" existing refineries for final processing (Corma et al., 2007; Solantausta, 2011). The main benefit of this approach will be capital cost savings by utilizing facilities and off-take infrastructure that has already been built. For example and as mentioned earlier, the USDA "Regional Roadmap to Meeting the Biofuels goals of the Renewable Fuels Standard" (2010) concluded that 527 new biorefineries would be needed to meet the requirements of the RFS 2, at a cost of about 168 billion USD (Weyen 2012). A big part of this capital cost could be avoided if biomass intermediates could be upgraded to biofuels using existing oil refinery equipment. It should be noted that, in the US, refinery utilization is expected to decrease as the US EIA predicts a reduction in refinery throughput over the next decade (EIA 2009). Another important trend that is projected for the next three decades is that refineries in the US and around the world will be producing less gasoline and more diesel and jet fuels (more middle distillates). This shift translates to refineries directing petroleum feed away from FCC units and towards hydrocracking units. According to the US EIA 2013 Annual Energy Outlook (EIA 2013), the already decreased utilization of FCCs (83% in use in 2011) in US refineries is expected to decline further and approach 62% in 2040. In contrast the US hydrocracking capacity is expected to increase from 1.8 million bpd in 2012 to 3 million bpd in 2040. More recently, the OPEC World Oil Outlook (2016) projected utilization of hydrocracking units to be in the low 80% range, through the period to 2040. In comparison, FCC unit utilization peaked at 81% close to 2020 due to short-term gasoline demand increase and then gradually down to 75% after 2030[68].

It has been suggested that oil refiners could either dedicate whole process units such as hydrotreaters exclusively to bio-oil processing or they could co-process bio-oils together with petroleum feeds (Corma et al, 2007, Egeberg et al., 2010). Dedicating whole refinery units to upgrading bio-oil derivatives would save capital costs and avoid complications of co-processing. However, candidate refinery units for biomass liquids processing such as hydrotreating and hydrocracking facilities are very large scale and as noted

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[68] https://woo.opec.org/images/woo/WOO_2016.pdf

earlier, they typically process around 100,000 barrels of fuel per day. Commercial pyrolysis facilities are usually envisioned to be about 30 times smaller at around 3,000 barrels per day. This is a scale large enough to benefit from economies of scale while small enough to avoid transporting bulky and wet biomass over prohibitively long distances (Stephen et al. 2010). Thus sourcing, transporting and utilising the biomass feedstocks that will be needed to feed even a small refinery unit will be challenging. Thus, co-processing is a more likely integration pathway than dedicating entire refinery units to biomass feeds. Co-processing also has the advantage that small amounts of biomass derived liquids can be blended with petroleum feeds to mitigate the problems that come with neat pyrolysis oil processing.

As mentioned earlier, neat pyrolysis oils cannot be readily co-processed with petroleum feeds as they typically contain up to 30% water and 40% oxygen. Thus, not readily miscible with the apolar petroleum liquids (Venderbosch and Prins 2011). As the high oxygen content of bio-oils also increases coking and deactivation of zeolite and HDO catalysts, they cannot be readily inserted in oil refineries before at least partial deoxygenation (hydrotreated). It will be important to deoxygenate "just enough" to meet the minimum requirements of the refinery as deoxygenation gets disproportionately costlier when approaching oxygen-free bio-oils (Ringer et al. 2006; Elliott 2007).

Once the oxygen content of the bio-oil has been reduced by hydrotreatment, it becomes a liquid hydrocarbon intermediate (such as hydrodeoxygenated oil, (HDO)) that can potentially be inserted into an oil refinery. As HDO bio-oils, even when partially deoxygenated, are unstable at 400 °C or 500 °C (temperatures that are often used in petroleum vacuum distillation) they cannot be directly inserted with crude oil at an early process stage of the refinery. Thus bio-oil insertion is likely to occur at the refinery's hydroprocessing (hydrotreatment and hydrocracking) or fluid catalytic cracking reactors. As described earlier, these two processes are similar to the processes used for hydroprocessing and zeolite cracking of neat pyrolysis oils in stand-alone setups. A simplified schematic showing HDO bio-oil insertion points (red arrows) within a typical refinery is outlined in Figure 15.
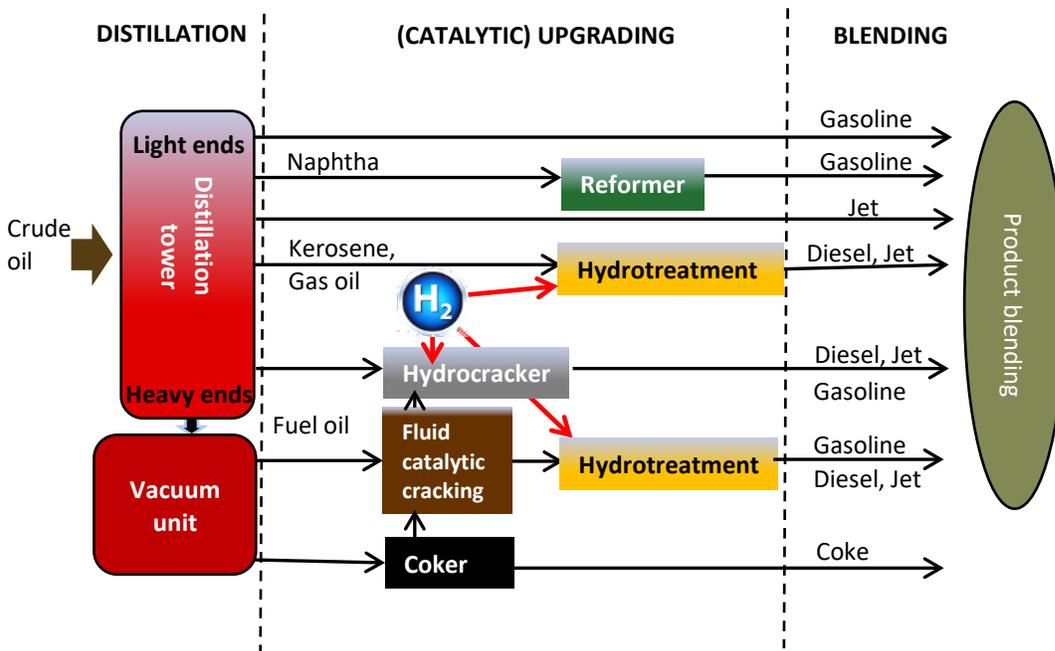
Figure 15 Refinery insertion points (red arrows) for HDO Bio-oils. Source: adapted from (US EIA, 2007)

It is important to clarify that the use of the term hydrodeoxygenated oil (HDO) is not well defined as it simply refers to a bio-oil that has been stabilized through hydrotreatment. However, the degree of hydrotreatment can vary markedly, largely depending on the co-processing insertion point and the blending ratio. The FCC insertion point can take more oxygen while hydrocrackers are far more sensitive to oxygen and other contaminants and the feed is usually hydrotreated before entering the hydrocracker.

3.10.1 Insertion of bio-oils/biocrudes in the fluid catalytic cracker

Recently Stefanidis et al. (2017) discussed the possible insertion of bio-oil/biocrudes into the fluid catalytic cracker. These authors suggested that increased coking and reactor plugging due to char and coke formation make raw bio-oil unsuitable for co-processing unless the bio-oil is first upgraded through hydrotreatment to remove oxygen. However, they also indicated that these findings might be a result of the experimental set-up as the conditions did not resemble a real FCC. They subsequently found that different conclusions were obtained when using a pilot scale FCC under more realistic conditions. In related work de Rezende Pinho et al. (2015, 2017) looked at the co-processing of bio-oil in the FCC after appropriate reactor modifications, including separate injection of bio-oil. However, other workers (de

Miguel Mercader et al. 2010) have argued that only the most reactive compounds and functional groups needed to be stabilised and that, consequently, up to 28% oxygen could be tolerated.

Despite these differences in opinion, there seems to be a general consensus that partial deoxygenation of bio-oil is probably required before insertion if potential suppliers are to meet the minimum requirements of the refinery. However, as mentioned earlier, complete deoxygenation of bio-oil is expensive since deoxygenation gets disproportionately costlier when approaching an oxygen-free status. (Ringer et al. 2006; Elliott 2007; Arbogast et al. 2017) Catalytic pyrolysis bio-oils and biocrudes from hydrothermal liquefaction are already partially deoxygenated and could potentially bypass intermediate steps prior to catalytic cracking. It should also be noted that many partially deoxygenated bio-oils and HTL biocrudes have very high viscosities, making pumping difficult (Choudhary and Phillips 2011; Elliott et al. 2015; Elliott 2007).

Earlier FCC-based trials which looked at co-processing bio-oil in blends with vacuum gas oil (VGO) demonstrated that lower H/C ratio products were produced when compared to processing VGO alone. (Corma et al. 2007; Lappas et al. 2009) It was also concluded that heavier (coke and tar) and lighter (gasoline and gases) fractions were produced at the expense of middle distillates while the gasoline produced was generally poorer in saturates and richer in aromatics (Lappas et al. 2009). Two related studies include, co-processing a mixture of 20% HDO bio-oil (at 20% oxygen) with petroleum VGO in an FCC (Fogassy et al. 2010), while de Miguel Mercader et al. (2010) co-processed an HDO bio-oil (28% oxygen) with a Long Residue heavy petroleum feed. Both of these studies reported a decrease in the coking propensity of HDO bio-oils when they were blended as compared to fossil feeds catalytic cracking. This was attributed to the transfer of hydrogen from the petroleum to the biomass feed during co-processing.

In other work, where FCC co-processing of raw bio-oils with a 51% oxygen content was tested (de Rezende Pinho et al. (2015, 2017)), the oxygen was primarily removed as H_2O, while CO yields were higher than CO_2 yields. Co-processing resulted in gasoline and diesel products with some renewable content, as determined by ^{14}C isotopic measurement. A 10 wt% blend of bio-oil resulted in a 2% renewable content in the total liquid product (de Rezende Pinho et al. 2015). It was also concluded that oxygen removal took place through hydrogen transfer from the fossil feed molecules. This resulted in a higher aromatic content

in the final products, with higher levels of phenolics found in the naphtha product. It is important to note the experimental set-up for this FCC demonstration study, in contrast to the many previous

laboratory/pilot scale tests, featured a circulating riser with different feed nozzles. This allowed the separate insertion of the bio-oil (at room temperature) at a lower point in the riser, compared with the temperature of the VGO at 220-280°C. It also resulted in lower coke formation than the FCC lab-scale test using Micro Activity Testing (MAT) where the feed was blended and heated prior to insertion into the reactor. Based on these types of results, de Rezende Pinho et al (2015) have suggested that lab-scale testing does not adequately predict the behaviour of co-processing of bioblends in an FCC, primarily because it is difficult to replicate real reactor conditions. Bezergianni et al (2018). came to a similar conclusion, although they thought the observation was mostly applicable to raw bio-oil cracking. However, in earlier work, Bryden et al. (2013)[69] found increased coke formation in spite of using a pilot-scale circulating riser reactor and modified feed delivery system. This was similar to the subsequent results reported by Zacher et al. (2015)[70] where changes in product yeilds were also reported, particularly a reduced gasoline yield.

Other related work has suggested that co-processing hydrogen deficient bio-oils with hydrogen-rich petroleum feeds can have a positive synergistic effect in mitigating the production of solid by-products (Stefanidis et al. 2017). This implied that the characteristics of a fossil feed will impact potential synergy, as hydrogen transfer between the fossil feed and bio-components takes place.

In summary, while catalytic cracking of raw pyrolysis oil is possible, when certain modifications are made to overcome miscibility problems, the processing of hydrodeoxygenated oils (HDO) and catalytic pyrolysis oils (CPO) is usually easier(Stefanidis et al. 2017).

3.10.2 Insertion of bio-oils/biocrudes into the hydrotreater

The lack of miscibility of bio-oils with the fossil feed is a key problem as hydrotreating cannot take place unless mixing takes place. However, as most studies on co-processed hydrotreatment have used model compound, the results have consequently been difficult to apply to real bio-oils (Bezergianni et al. 2018).

As mentioned earlier, hydrotreatment units are sensitive to oxygen and unlikely to be used to process bio-oils with an oxygen content that exceeds about 5% at blending ratios of less than 10% (Solantausta 2011). Depending on the molecular weight distribution of the bio-oil, cracking of molecules may be required,

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[69] https://www.energy.gov/sites/prod/files/2014/05/f15/biomass13_habib_2-d.pdf
[70] https://www.energy.gov/sites/prod/files/2015/04/f21/thermochemical_conversion_zacher_242402.pdf

although this is not usually carried out in the hydrotreater as mild conditions are used. However, hydrocracking typically follows hydrotreating in an oil refinery and it is even less tolerant to oxygen than hydrotreatment (due to higher pressures and temperatures). There is limited experimental data on co-feeding of real bio-oils with petroleum feeds in hydrotreating units. This is not unexpected as problems such as increased coking and catalyst deactivation, increased hydrogen demand and potential irregular hydrogen pressure drops inside the reactor can be anticipated(Butler et al. 2011).

It is apparent that both FCCs and hydroprocessing refinery units can accept bio-oils that have been partially deoxygenated (HDOs). However, the two facilities differ in their relative suitability for biofeed insertion (Table 13). It has been shown that FCCs can handle lower grade (up to 20% oxygen) HDOs without the need for hydrogen. However, this results in lower conversion yields, large amounts of waste energy production and lower value end products (low H/C ratio) which will contribute mostly to marine and bunker fuel blendstocks. In this regard the FCC can be viewed as the "workhorse" of bio-oil co-processing. Alternatively, hydroprocessing could be considered the refinery's "boutique" upgrading unit as it requires more deoxygenated bio-oil co-feed (max of 3-5%) and it is designed to produce higher grade diesel and jet fuels.

Table 13 Comparison of FCC and hydroprocessing as refinery co-processing platforms for bio-oils.

	FCC (Fluid Catalytic Cracking)	Hydroprocessing (hydrotreating followed by hydrocracking)
Tolerable oxygen content in bio-oil feed	Up to 20% (<5% blend)	No more than 3-5%
Pre-refinery hydrotreatment	Single stage/mild	Two-stage/severe
Hydrogen use (NL / L of bio-oil)	ca. 300	>800
Yields	Low (10-15% in standalone)	High (25% in standalone)
Downstream contamination risk with oxygenates	High	Low
Opportunity for power generation through coke combustion	High	Low
Chemistry of product	Favors aromatics (low H/C_{eff} ratio)	Favors short paraffins (high H/C_{eff} ratio)
Fuel pool (most contribution)	Gasoline and Marine fuels	Middle distillates: Diesel and Jet fuels

Source: (adapted from Solantausta, 2011)

As has been described in detail, the production of bio-oil intermediates via pyrolysis is relatively inexpensive and it can be decoupled from the subsequent upgrading steps thus facilitating feedstock delivery logistics (e.g. bio-oil is more energy dense and should be cheaper to transport than the original biomass feedstock). However, the resulting bio-oil is physicochemically disparate from petroleum liquids and thus the greatest costs and technological challenges of this platform are in upgrading the bio-oil to petroleum- equivalent transport fuels. It should be noted that upgrading costs have been estimated to account for about two-thirds of the capital expenses and about half the operating expenses. Hydroprocessing has many advantages as an upgrading technology, not least among which is that it can efficiently elevate the H/C ratio of the bio-oil prior to final conversion to transport fuels. Oil refinery FCC and hydrotreating units can be leveraged by bio-oil upgrading processes, although the insertion of insufficiently deoxygenated bio-oils poses numerous technical challenges (coking, catalyst deactivation, corrosion) and will cause a reduction in the H/C ratio of the refinery's products. However, the significant capital cost savings as well as some synergistic benefits (coking and viscosity reduction) warrant the continued interest in co-processing partially upgraded bio-oils with petroleum feeds inside oil refineries. Recent work in the pyrolysis area has suggested that the greatest benefits in upgrading bio-oils are not necessarily in maximizing oxygen removal but rather in first removing the most unstable oxygenated

compounds by way of a mild hydrotreatment step. The technical area that could have the biggest impact on facilitating improved bio-oil upgrading, as implied by the assumptions in the various techno-economic models, is increasing the selectivity and lifespan of the hydrotreating catalysts that are used.

3.8 GASIFICATION-BASED BIOFUEL PRODUCTION

The objective of thermochemical liquefaction technologies is to maximised production of a liquid biocrude that can be upgraded into drop-in biofuels. However, gasification produces mainly gas from solid biomass, together with small amounts of liquids and char. Gasification is typically conducted under conditions of high temperature and pressure using air, oxygen or steam as a gasifying agent to convert biomass to a low to medium energy gas known as synthesis gas or "syngas". In a second stage, the synthesis gas is converted into liquid drop-in biofuels through two types of processes, namely Fischer-Tropsch synthesis or methanol to gasoline. However, prior to synthesis, the syngas needs to be cleaned so that it consists mainly of H_2 and CO, the starting material for Fischer-Tropsch synthesis.

Although gasification is extensively used it is mainly for heat and energy generation with the production of liquid fuels from syngas much less prevalent. While liquid fuels have been produced at a large scale based on the gasification of coal or from natural gas, the use of biomass feedstocks to produce biofuels in this manner has been slow to commercialise. A major challenge has been syngas cleanup, based on biomass gasification, in addition to adding substantial cost to the overall process. The type of gasifier technology used will also have a significant impact on the quality of the syngas produced and the extent of cleanup required. Plasma gasifiers produce very clean syngas, but the cost of the reactor and the high temperatures required, make this technology less attractive. Thus, biofuel projects such as the one proposed by Solena and British Airways, likely failed to materialise due to the high cost of the gasifier. At the other end of the scale, fixed bed gasifiers are much cheaper to build and operate yet produce a poor quality syngas that contain high levels of tars that are difficult to clean up. Other gasifier technologies include various fluidized bed reactors and entrained flow reactors. However, one of the key requirements when operating an entrained flow gasifier is the need for small particle size (1mm). Although this is generally not an issue when using feedstocks such as coal, that can be pulverised, it is much less suitable for woody, fibrous biomass where extensive size reduction can add significant costs. Consequently, fluidized bed reactors tend to be the gasifier technology of choice for many companies. While the bubbling fluidized bed reactor produces high tar levels, combining the gasification with steam reforming, as

demonstrated by Fulcrum Bioenergy, reduces tar levels and boosts hydrogen concentration in the syngas through the water gas shift reaction.

Another issue is the scale that will likely be required to make gasification-based processes economic. Although the use of coal or natural gas as the feedstock allows facilities to operate at a very large scale, biomass has a low energy density, making transport of the feedstock at a large scale an economic and logistic challenge.

Syngas has less than half the energy density of natural gas (natural gas contains about 36 MJ/Nm^3 whereas biomass syngas contains only about 4-18 MJ/Nm^3 (4 MJ/Nm^3 for air blown and 18 MJ/Nm^3 for steam blown gasification (Bain 1992)). The quality of a syngas for synthesis applications is often measured by its H_2/CO ratio. A higher ratio typically indicates a greater energy density and therefore better potential for upgrading to drop-in biofuels.

Four main reactions take place during gasification to form syngas:

- o Water Gas $\quad$ C + H$_2$O $\quad \rightarrow$ CO + H$_2$
- o Boudouard $\quad$ C + CO$_2$ $\quad \rightarrow$ 2CO
- o Water-Gas-Shift $\;$ CO + H$_2$O $\rightarrow$ CO$_2$ + H$_2$
- o Methanation $\quad$ CO + 3H$_2$ $\rightarrow$ CH$_4$ + H$_2$O

The chemical composition of the produced syngas depends on the relative prevalence of the reactions taking place at the reduction step of gasification. For example, when adding steam to the reactor, the water-gas-shift (WGS) reaction is favoured and more hydrogen is generated which boosts the H_2/CO ratio of the resulting syngas. Alternatively, when hydrogen is fed to the reactor, the methanation reaction is favoured and the generated syngas is rich in CH$_4$ (useful for the production of synthetic natural gas) (Bain and Broer 2011).

3.8.1 Gasifier types

Gasification relies on reactor configurations that maximize heat transfer through the biomass particles. Although the reactors used for gasification are similar to the ones used for pyrolysis, they typically operate at higher temperatures (800 – 1000 °C) and pressures from 1 to 50 bar. Four types of reactors are typically used for biomass gasification including fixed bed, fluidized bed, entrained flow and plasma gasifiers.

The fixed bed reactor is the simplest and most established design and it tends to be found in older, smaller scale systems. There are two types of fixed bed reactors and, depending on whether the gases are blowing countercurrent or concurrent to the biomass feed, they are called updraft or downdraft fixed bed reactors. Fixed bed reactors are typically quite simple to build and operate. However, their use is limited by poor heat and mass transfers, mainly due to the formation of preferential channel flows within the fixed biomass bed (Swanson et al. 2010). They are also not suitable for large scale applications.

By increasing the volumetric gas flow of the air blown through the fixed bed, turbulence agitates the particles of the bed (thus 'fluidizing' the bed) and the reactor becomes a fluidized bed gasifier. In fluidized bed gasifiers the bed particles are composed of gasifying biomass as well as of very hot and small inert particles which greatly improve the heat transfer throughout the gasifying biomass particles. There are two types of fluidized bed reactors, the Bubbling Fluidized Bed (BFB) and the Circulating Fluidized Bed (CFB) reactors. These types of reactors have been described earlier in the pyrolysis section. The difference is that, for effective gasification, the operating temperatures are much higher than are used for pyrolysis since the objective is to maximize production of permanent gases as opposed to condensable vapors. Compared to fixed beds, fluidized beds generally have higher carbon conversion efficiencies and they tend to be more easily scaled-up (Swanson et al. 2010; Bain and Broer 2011). The use of a fluidized bed reactor configuration has been the preferred choice for several of the companies that are currently scaling up the gasification technologies.

Enerkem is a Canadian company that has developed its own gasification technology to produce methanol and ethanol through catalytic condensation of biomass (or municipal solid waste, MSW) derived syngas. The Enerkem platform involves a fluidized bubbling bed gasifier followed by cyclone filtration and wet scrubbing of the syngas. The clean syngas is then catalytically converted to mixed alcohols. A 5 MLPY (1.3 MGPY) demonstration facility has been operating at Westbury, Quebec since 2009, gasifying old electricity poles and sorted MSW to make syngas (since 2009), methanol (since 2011) and ethanol (since 2012). A second 38 MLPY (10 MGPY) facility has been operating in Edmonton, Alberta since 2014 and has used post-sorted MSW as the feedstock. A third 38 MLPY (10 MGPY) facility at Varrennes, Quebec is under

construction, with a joint venture between Enerkem and Canadian corn ethanol company *Green Field Ethanol Inc* also proposed[71].

Another company, ThermoChem Recovery International, Inc. (TRI) produces steam reforming gasification systems which it has licensed to different companies. A TRI gasifier has been used by Norampac in its Trenton, Ontario, Canada facility to gasify black liquor from their paper mill. TRI is also the gasification technology provider for two separate DOE-funded biorefinery projects (NewPage Corporation and Flambeau River Biofuels) which will convert the syngas to FT waxes and diesel and provide tailgas to offset natural gas in the lime kiln[72]. TRI's process demonstration unit in Durham, North Carolina (4 dry ton/day) proved conversion of biomass and municipal waste to biofuels and biochemicals over 10,000 hours of steam reforming and gas clean-up and 4,500 hours of biofuels production[73]. TRI has demonstrated the FT products can be upgraded to ASTM certified fuels and supported the demonstration of TRI's technology in providing renewable fuels for US Department of Defense. Fulcrum Bioenergy licensed TRI's gasification technology to convert pretreated municipal solid waste to syngas. The Sierra Biofuel Plant located in Storey County, Nevada and is expected to process 175,000 tons of MSW annually and produce 10.5 million gallons per year of "syncrude" which will be further upgraded to transportation fuels by an Andeavor refinery (formerly Tesoro). Phase 1 of the feedstock processing facility was completed in 2016 and phase 2 of converting the MSW to syncrude is under construction with planned commencement in 2020[74].TRI is also Velocys' preferred supplier of gasification system for their biomass-to-liquids (BTL) plants[75].

Repotec has collaborated with the pulp and paper technology provider Metso to provide the gasification technology for the *GoBiGas* facility in Goteborg Sweden. Phase 1[76] of this ground-breaking facility could produce 20 MW biomethane, in addition to 5 MW district heating. The high purity methane will be produced using Haldor Topsoe technology and it will be fed into a specialized grid catering to a local fleet of 16,000 automobiles yearly. The demonstration plant was commissioned in 2013 and started operation

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[71] http://demoplants.bioenergy2020.eu/

[72] http://www.biofuelsdigest.com/bdigest/2014/02/23/thermochem-recovery-international-tri-biofuels-digests-2014-5-minute-guide/

[73] http://tri-inc.net/deployments/

[74] http://fulcrum-bioenergy.com/facilities/

[75] https://www.velocys.com/establishment-of-a-strategic-alliance-with-tri/

[76] https://www.svebio.se/app/uploads/2017/05/Holmquist_Lars_ABC17.pdf

in 2014. The facility received EU NER300 funding support for the phase 2, a 80-100 MW commercial plant, but this endeavour was subsequently cancelled[77]. More recently (2018) the demonstration facility was mothballed[78].

An entrained flow reactor is a type of gasifier where biomass is fed in the form of very fine particles (or atomized pyrolysis liquids) which are entrained into a high-velocity stream of air or oxygen (Bain & Broer, 2011). These streams are fed from the top of the hot reactor where the temperatures are high enough (about 1300 °C) that the entrained biomass particles are gasified before they reach the bottom of the reactor. Entrained flow (EF) gasifiers have been developed for use with coal by companies such as Shell, Texaco, Conoco Philips (Bain and Broer 2011) and have had limited application with biomass feedstocks. One of the reasons is that feed preparation costs are much higher for biomass than they are for coal and their use also involves extensive drying and size reduction (<1mm) (Swanson et al. 2010). The advantages of using entrained flow gasifier are that the produced syngas is clean and tar-free due to thermal cracking taking place at the higher temperature and conversion close to 100% is achieved. However, the requirement to reduce the size of the biomass feedstock is highly energy intensive plus the potential corrosion of the gasifier lining is also likely inhibiting entrained flow gasifier deployment.

Another company that has been engaged in developing gasification is Thyssen Krupp Uhde. Among Uhde's gasification platforms the most relevant to biomass are the HTW™ (High temperature Winkler) and PRENFLO™ (entrained flow) reactors[79]. The HTW process is a CFB design which was developed in the early 1970s by Rheinbraun (now RWE). This process is a pressurized version of an even older CFB technology which was originally developed by the German, Fritz Winkler (hence the name) in the 1920s. The technology has been incorporated into various pilot plants at operating pressures that ranged from 1.5-27 bar, temperatures between 700-950 °C and carbon conversion efficiencies (gasification step only) that can reach 95%. Uhde has recently purchased the HTW technology from RWE and applied it to various projects. Most of these projects are at the design and development stage in various locations around the world including Japan, Sweden, India and Australia (E4tech, 2009).

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[77] http://www.biofuelsdigest.com/bdigest/2018/06/27/gobigas-the-digests-2018-multi-slide-guide-to-advanced-biofuel-production-via-gasification/8/
[78] https://bioenergyinternational.com/research-development/goteborg-energi-winds-gobigas-1-project-advance
[79] https://www.globalsyngas.org/uploads/eventLibrary/GTC-2012-4-3.pdf

Another Uhde gasification technology relevant to biomass is the entrained flow gasification platform called PRENFLO. This platform, originally developed for coal gasification, is well suited for a torrefied biomass feed and it is at the heart of a BioTfuel project with a budget of €178.1 million, including €33.2 million state funding[80]. The BioTfuel consortium hopes to produce FT drop-in biofuels derived from the gasification of multi-feedstocks including wood, straw, coal, petcoke and liquid residues. Wood and straw will first be torrefied and then milled before entering into the gasifier. Coal and petcoke need to be milled while liquid residues can be directly feed into the gasifier[81]. The biomass pretreatment and torrefaction will occur at Sofiprotéol's site in Venette, France with the subsequent process steps (gasification, syngas clean-up and synthesis) performed at Total's site in Dunkirk, France.

An alternative strategy to preprocessing biomass is the approach taken by companies such as Germany's KIT ("bioliq" technology). They propose feeding entrained flow gasifiers with pyrolysis slurries as opposed to comminuted biomass. This approach results in an improved feed for entrained flow gasifiers and also offers the option to decouple the conversion of biomass to bioslurries from the central gasification plant in terms of space, time and synchronization.). The main principle is to produce energy dense biomass slurries in separate auger-pyrolizers and then feed these "bioliq SynCrude" slurries into a central entrained flow gasification facility. The resulting syngas is purified using Lurgi's Rectisol and Purasol processes. Assessment has been underway since 2006 using a $2MW_{th}$ bio-slurry pilot plant and in 2007 a second $5MW_{th}$ facility was built that included an 85 bar gasifier. The second phase was completed on February 2013 with the plant producing high quality, almost "tar-free", biomass syngas (KIT 2013). The bioliq pilot plant at KIT has been running successfully since 2014 and all of the stages of the process have now been interconnected. These include Flash pyrolysis, high-pressure entrained flow gasification, hot gas cleaning and synthesis (DME and drop-in fuels). In March 2015, Air Liquide provided key technologies for the pyrolysis of biomass and gas synthesis as well as the oxygen supply needed for the gasification process[82].

Although plasma gasifiers have a similar structure to entrained flow reactors they operate using plasma torches at extremely high temperatures of 1500 °C – 5000 °C (atmospheric pressure). Although they are

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[80] http://www.ifpenergiesnouvelles.com/News/Press-releases/Inauguration-of-the-BioTfueL-project-demonstrator-in-Dunkirk-2nd-generation-biodiesel-and-biokerosene-production-up-and-running
[81] https://www.globalsyngas.org/uploads/downloads/2016-4-2-ThyssenKrupp-KarstenRadtke.pdf
[82] http://www.etipbioenergy.eu/value-chains/conversion-technologies/advanced-technologies/biomass-to-liquids/btl-demonstration-projects-in-europe

costly to operate, they are able to produce a very high quality syngas which needs little further cleanup (E4tech, 2009). In this process, the biomass is converted to syngas and the inorganic ash is vitrified to inert slag. Projects that have proposed using a plasma gasifier have been based on municipal solid waste as a feedstock. However, the high cost has been prohibitive. The company Solena cancelled their project with British Airways while Fulcrum Bioenergy, who initially selected a plasma gasifier technology, switched to a bubbling fluidized bed technology.

3.8.2   Syngas cleanup

The "clean up" of syngas based on gasification of biomass is one of the key aspects of biofuel production using this technology. Raw biomass syngas is recovered along with numerous impurities such as small char particles, tar vapors as well as volatile nitrogen and sulfur compounds. Char is entrained in the syngas and it is comprised of non-volatilized biomass as well as ash. The tar component is formed during the polymerization of biomass vapors and it can stick to reactor walls and catalysts causing clogging and deactivation. Sulfur and nitrogen gases are derived directly from the biomass feed and those components are deleterious to downstream processes as they cause NOx and SOx emissions upon combustion and they can also "poison" the Fischer-Tropsch catalysts (Dayton et al. 2011).

When the syngas is simply burned, these impurities are of lesser concern. However, when the syngas is used for more "sophisticated" applications such as internal combustion (IC) engines, gas turbines and Fischer-Tropsch (FT) synthesis, exhaustive cleanup is required. For internal combustion (IC) engines to operate effectively, particulates, tars and acids must all be at concentrations below 50 mg/Nm^3. For FT synthesis the particulate matter must be less than 0.03 mg/Nm^3. Unfortunately, for most raw syngases the contaminant concentrations typically exceed these limits by some orders of magnitude. This is especially true for fluidized bed gasifiers which, when compared to entrained flow gasifiers, operate at lower temperatures and circulate the gas through beds that are rich in fine char solids. As summarised in Table 14, a Circulated Fluid Bed (CFB)-derived syngas typically contains about 10,000 mg/Nm^3 of either char or tar particles, Bubbling Fluidised Bed (BFB) up to 43,000 mg/Nm^3 and downdraft fixed beds as much as 30,000 mg/Nm^3.

Table 14 Char and Tar content of biomass syngas from different reactors

Reactor type	Tar content (mg/Nm³)	Char content (mg/Nm³)
Updraft	50,000	nd
Downdraft	1,000	9,300 – 30,000
BFB	10,000	1,040 – 43,610
CFB	10,000	1,700-13,100
Specification for IC engines	<50	<50
Specification for FT synthesis	<0.02	< 0.02

Source: Data from (Milne et al. 1998; Carpenter et al. 2010; Drift et al. 2001; Meehan 2009; Wander et al. 2004; Bain and Broer 2011)

There are various ways to reduce the accumulation of these contaminants during gasification but they come at a price. For example, at high gasification temperatures (e.g. >1200 °C) the formation of char and tar is reduced and the production of permanent gases is favoured. However, high temperature gasifiers such as plasma are costly to build and operate. Similarly the introduction of steam has been shown to reduce the buildup of tar by reforming it to H_2 and CO. However, steam can act as a heat sink and it can significantly compromise the heat balance and overall efficiency of the gasification plant. Higher air to fuel ratios cause more oxidative conditions and they are beneficial in reducing the char and tar content of syngas but these conditions favour more full oxidation of gases to CO_2, thus recovering less combustible gases such as CO. Pure oxygen can be used instead of air in order to improve the specificity of the gasification reaction while also reducing the nitrogen contaminants coming from atmospheric air. However, the isolation and purification of oxygen weighs significantly on the economics of the facility (Mueller-Langer et al. 2007; Bain and Broer 2011; Swanson et al. 2010). Clearly, a compromise must be found between these trade-offs in order to strike the optimal quality syngas for each given application.

The ash content, another significant contamination in syngas, is largely dependent on the amount of inorganics in the initial biomass. As noted earlier, herbaceous and agricultural biomass tends to be higher in inorganics than wood derived biomass. Alkaline components of ash such as calcium and potassium are particularly undesirable since they are known to lower the overall melting point of biomass, thus promoting slagging at lower temperatures (Hayes 2013; Swanson et al. 2010).

Even if the process is optimised to minimize syngas impurities by adjusting gasification conditions, some cleanup is always needed. Syngas cleanup is one of the most expensive steps of a gasification biofuel platform. This typically involves various sequential steps that follow the gasification reactor including gas cyclone removal of most of the particulate matter above 10 μm and further removal of the smaller particles by more costly methods such as wet scrubbers or electrostatic precipitators (ESPs) (Dayton et al. 2011).

Tars are particularly problematic for Fischer-Tropsch (FT) fuel synthesis as they can irreversibly deactivate the catalysts downstream. Tars are typically removed by one of the two main strategies of wet scrubbing at low temperatures or cracking at high temperatures. Wet scrubbing involves significant cooling of the gas as well as the generation of wastewater streams that are contaminated with potentially toxic tar components which must be treated prior to disposal. As hot gas cleaning occurs at temperatures higher than the gasification temperatures (e.g. 1200 °C) the added energy requirements, including the need to extensively cool the gas down prior to FT processing, can compromise a facility's economic viability (Speight and Ancheyta 2007). Another cleanup option that has attracted research attention lately is the catalytic conversion of the tars in the gasifier outlet via steam reforming (Bain et al., 2014). The primary objective of tar control strategies is to either eliminate tars or to at least bring their dew point below the operating temperatures of the ensuing processes such that tar deposition is minimized. For more detail on the various syngas cleanup and conditioning technologies proposed, the reader is referred to a recent comprehensive reviews by Dayton et al. (2011), Woolcock and Brown (2013), Abdoulmoumine et al. (2015).

Gasification yields tend to be lower than desired as much of the original carbon is oxidized to generate heat. Only about half of the carbon is converted to usable CO while the other half is oxidized to CO_2 (Hayes, 2013). However, it has been recently demonstrated by researchers at the Universities of Massachusetts and Minnesota that the addition of methane to the gasification reaction can substantially enhance gasification yields. As methane has a high H/C ratio of 4, the hydrogen from the methane reacts with the CO_2 to form H_2O and CO (Hayes, 2013).

3.9   SYNTHESIS OF FUELS FROM SYNGAS

Syngas can be condensed into hydrocarbon liquids that can be used for biofuels and chemicals (Dayton et al., 2011). This condensation has to be selective and produce the targeted hydrocarbons, thus, specialized catalysts must be employed. The types of fuels and chemicals that syngas can be condensed to are summarised in Figure 16. These catalytic condensation reactions convert the syngas molecules (H_2 and CO) into larger molecules to produce energy dense liquids. The choice of targeted chemicals and the efficiency of each of the conversions depend on the choice of catalyst, condensation conditions used and the H_2 to CO ratio. More important than all of the above aspects is the level of contaminants in syngas which must be very low and preferably less than about 10 mg/Nm^3. Sulfur in particular is "poisonous" to FT catalysts and must be at concentrations that do not exceed 2 mg/Nm^3 (Dayton et al. 2011). The syngas catalytic condensation pathways that are most relevant to drop-in transport biofuels are the methanol to gasoline (MTG) and Fischer-Tropsch (FT) processes.
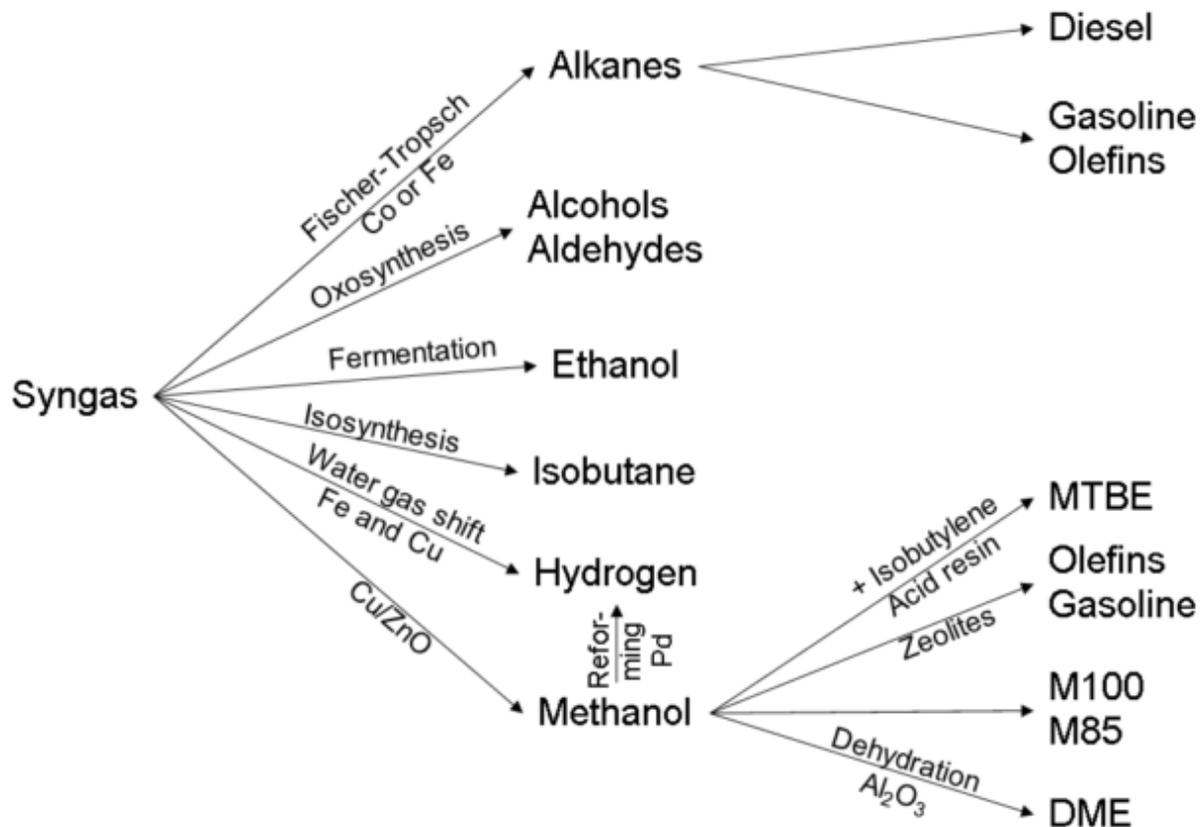

Figure 16 Main Syngas Conversion Pathways. Source: (Huber et al. 2006)

3.9.1 Methanol to Gasoline processes

The first step in this process involves the exothermic conversion of the syngas to methanol, which is a commercial technology. As long as the syngas is pure and it contains the required ratio of hydrogen to carbon monoxide, the conversion takes place in the presence of relatively inexpensive $Cu/ZnO/Al_2O_3$ catalysts at temperatures that range between 220-275 °C and pressures of 50-100 bar. Under these conditions the catalyst can last as long as 2-5 years (Swanson et al., 2010). Although the *per pass* conversion efficiency is typically about 25%, Wender (1996) has shown that up to 99% conversion can be achieved with gas recycle. The core reaction of this conversion is the reaction of one molecule of CO with two molecules of H_2 to form one molecule of methanol.

$CO + 2H_2 \rightarrow CH_3OH$
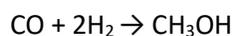
Methanol is a liquid fuel but not a drop-in transportation fuel. However, it can be turned into a drop-in gasoline equivalent using the methanol-to-gasoline process (MTG). This process was first developed and patented by Mobil Oil Corporation (now Exxon Mobil) in the 1970s. The process entails two steps. In the first step, methanol is dehydrated over an alumina catalyst at 300 °C and 27 bar, to form a mixture of dimethyl-ether (DME), methanol and water. In the second stage, this mixture reacts over a zeolite catalyst (359°C and 20 bar) and is further dehydrated to gasoline range hydrocarbons (44 wt%) and water (56 wt%) (Phillips et al. 2011; Swanson et al. 2010).

The efficiency of the process can be improved by stopping the reaction after the first stage since dimethyl ether (DME) can be used as a truck fuel (high cetane number). Dimethyl-ether is a gas at room temperature so it would have to be compressed before it is fed to an automobile engine (Swanson et al. 2010; Phillips et al. 2011).

3.9.2 Fischer-Tropsch processes

In 1923 Franz Fischer and Hans Tropsch identified catalysts that can condense carbonaceous gases to alcohols. The process was patented and named "synthol". The main motivation for this research was the scarcity of petroleum fuel in post-world war one Germany. The process was further developed to produce non-oxygenated liquid hydrocarbons as feedstocks for fuels and chemicals using improved catalyst formulations. This process became known as Fischer-Tropsch Synthesis (FTS). The process has undergone continued investigation and optimisation and it has since been adapted for a diversity of feedstocks including biomass.

Fischer-Tropsch synthesis can use syngas derived from any source including biomass, coal or natural gas and it can produce precursors for a wide range of drop-in chemicals and fuels. As long as the syngas is treated and conditioned properly and there is a good H_2/CO ratio, functional and chemical equivalence can be achieved between the syngas derived from these disparate feedstocks. However, it is more difficult to achieve the same level of syngas purity from biomass as from natural gas. Thus, it is possible to scale-up biomass-based FT processes by leveraging the know-how and facilities of existing natural gas and coal gasification FTS plants. The FTS reaction takes place over specialized catalysts and is essentially a dehydration reaction that it is highly exothermic (Swanson et al. 2010). The basic reaction is represented in the equation below:

$CO + 2.1\ H_2 \rightarrow$ - (CH_2) - + H_2O (delta Hr (227 °C)   - 165 kJ/mol

The catalyst surface acts as an "anchor" upon which the carbon monoxide and hydrogen adsorb (see Figure 17). The chain growth begins once the carbon monoxide has been broken down, enabling the coupling of carbon and hydrogen and the separation of oxygen (which leaves as a water molecule - dehydration). Chain growth continues by adding further CO and H_2 until the newly formed hydrocarbon molecule is desorbed from the catalyst surface.

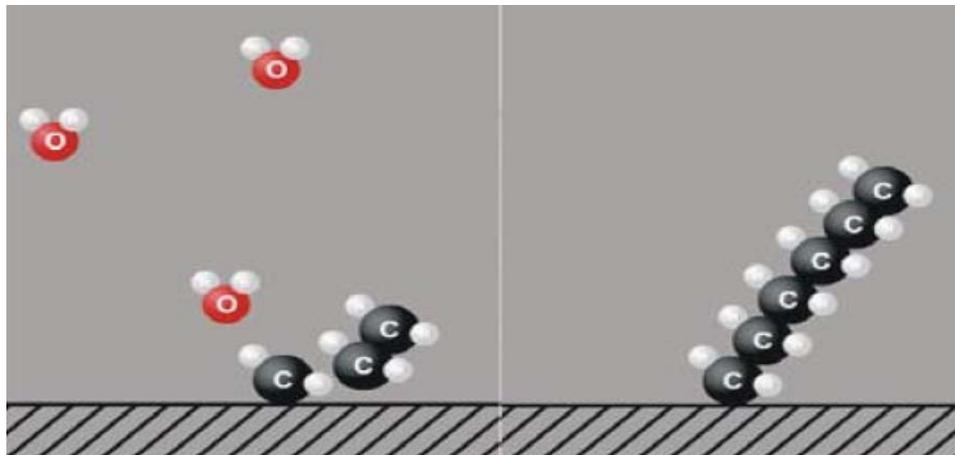*Figure 17 Simplified representation of Fischer-Tropsch chain growth on a catalyst surface. Source:* (Blades et al. 2005)

The pressures used during the FT process range from 10-to-40 bar and the nature of the hydrocarbons produced is influenced by the temperatures and catalysts used. Higher temperatures (300 – 350 °C) and iron catalysts produce gasoline, while lower temperatures (200 -240 °C) and cobalt catalysts produce

diesel and waxes. The distribution of heavier and lighter hydrocarbons can be estimated by employing the Anderson-Schulz-Flory probability model in which longer chain hydrocarbons form as the temperature decreases. The ratio of H_2 to CO also influences the product distribution with high ratios favouring the formation of lighter hydrocarbons. Iron catalysts favour the Water Gas Shift (WGS) reaction such that the H_2/CO ratio is increasing. With cobalt catalysts, WGS is not favoured and it has to be performed separately in order to achieve the desired high H_2/CO ratio (E4tech 2009).

The choice of catalyst used is important for effective Fischer-Tropsch Synthesis (FTS). The group VIII transition metal oxides are regarded as good CO hydrogenation catalysts, based on the three main performance characteristics of lifetime, activity and selectivity. Lifetime largely depends on the quality of the syngas. Prime quality natural gas-derived syngas catalysts have been reported to last up to 3-5 years. The most active metal catalysts for FTS, ranked in order of activity, are Ru>Fe>Ni>Co. Ruthenium catalysts are the most active, but they are considerably more expensive than the iron catalysts and about 100 times more expensive than Nickel and Cobalt. Nickel is a methanation catalyst and does not have the broad applicability in FTS that other FT catalysts have. Iron has Water-Gas-Shift (WGS) activity but is an acidic catalyst and promotes carbon deposition and coking, resulting in lower yields and reduced catalyst lifetimes. Cobalt is more alkaline and although about 200 times more expensive than Iron it produces higher yields and provides for longer catalyst lifetimes. However, it has low WGS activity and needs a separate WGS step to boost the H/C ratio of the feed to >2. Finally, as well as being highly active, a catalyst must also be selective in promoting the reactions that are most desirable. For example, Iron/manganese/potassium catalysts have shown selectivity for C_2-C_4 olefins as high as 90% (Bain and Broer 2011).

It is also recognised that temperature control is crucial for effective Fischer-Tropsch synthesis (FTS). The FTS reaction is so exothermic that the heat generated can irreversibly deactivate the catalyst if it is not dissipated. Another reason why FTS temperatures must be kept under tight control is that, as the temperature approaches 400 °C, the methanation reaction is favoured. However, this is only desirable when the target of the conversion is to make synthetic natural gas (SNG). Therefore, FT synthesis reactor design must be such that the heat from the reactors can be readily dissipated. Various reactor designs such as tubular and slurry-based have been developed for this purpose (Swanson et al. 2010).

Overall, the FTS-from-biomass process involves four major steps (Figure 18). These steps are; a) syngas production, b) syngas cleanup, c) FT synthesis and, d) product upgrading. As is apparent from the

schematic in Figure 18, each one of these steps is performed at different temperature and pressure conditions. From an energy balance and economic viability perspective, the high pressure and temperature fluctuations throughout the process are of some concern. The high pressure consumes energy and it also results in greater capital expenditures as the gas compressors needed to feed the pressurized reactor vessels are among the most costly pieces of equipment in a gasification plant (see subsequent techno-economic section). Similarly, heating and cooling cycles incur undesirable energy "losses". If the syngas is cleaned of tars through thermal cracking at >1300 °C, it then has to be cooled down to about 300 °C and pressurized to >30 bar before it enters the FT synthesis reactors. If, on the other hand, the tars are removed by way of quenching, they have to be cooled down before they enter the wet scrubbers and again heated and pressurized before they enter the FT synthesis reactors. All of these heat-cool and compression operations are costly and they add significantly to the capital cost of biomass to liquids facilities. There is ongoing research and development to improve gasification platforms so as to minimize these costly fluctuations in temperature and pressure.
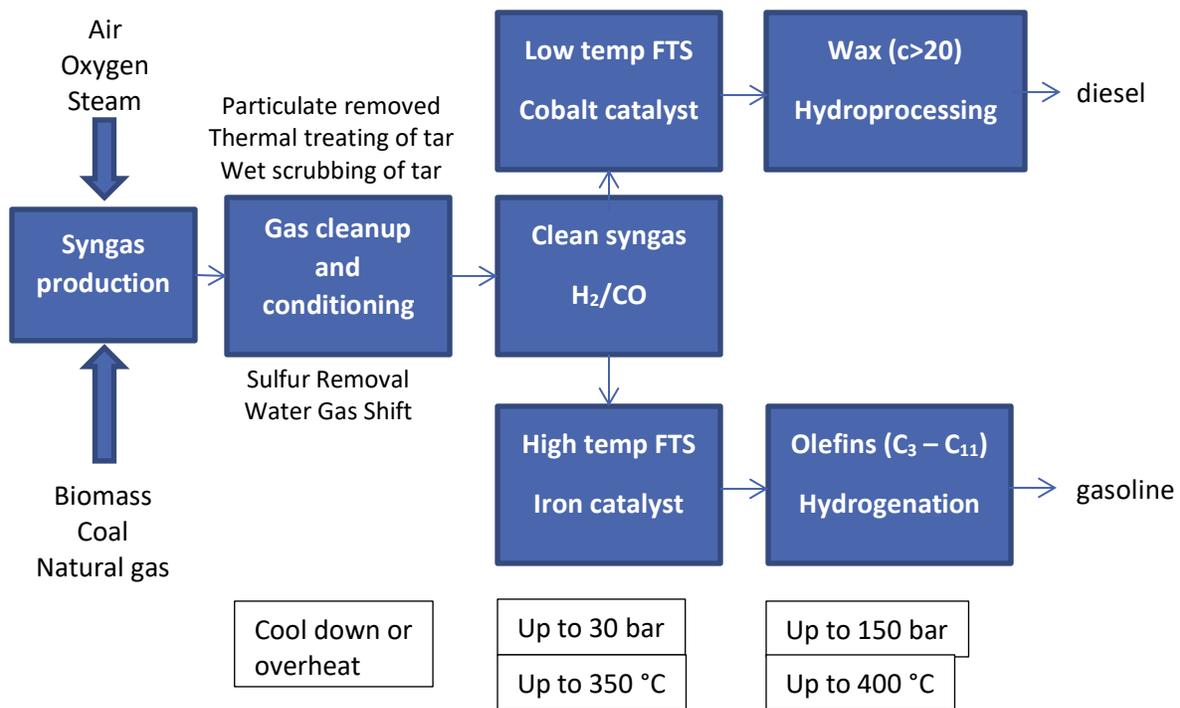

Figure 18 Simplified schematic of the overall biomass gasification to FT diesel and gasoline process.

Source: Adapted from (Bain and Broer 2011)

After the production of FT liquids, further upgrading is required to produce finished fuels, most likely through hydrotreating, hydrocracking, isomerisation and fractionation. This can easily be carried out at existing petroleum refineries and this highlights the overall importance of refinery integration as a key to drop-in biofuel expansion. For example, the Karlsruhe Institute of Technology (KIT) has proposed the co-location of its bioliq® process (a "hub and spoke" pyrolysis-then-gasification approach) with an oil refinery (Dahmen et al. 2012). The core gasification-FT facility would be located next to a petroleum refinery where the final hydroprocessing steps would be performed without the need to build separate hydroprocessing reactors. As FT liquids consist of a range of hydrocarbons, fractionation through distillation might also be carried out. The quality of FT liquids, including low oxygen content, poses a very low risk for the refinery but very limited information is available publicly to demonstrate effective integration.

The Fischer-Tropsch process is currently being operated at an industrial scale by two main fossil fuel companies in South Africa (Sasol) and in Malaysia and Qatar (Shell), using natural gas and coal as feedstocks. The world's first commercial-scale gas-to-liquid (GTL) plant based on FT synthesis was completed in 1993 by Shell in Bintulu, Malaysia and continues producing about 15,000 barrels per day (bpd). The previously discussed Sasol plant produces 160,000 barrels of FT-diesel per day from coal syngas to provide 41% of South Africa's transport fuel requirements. Sasol has also converted one of its coal-to-liquid (CTL) facilities to accept natural gas from Mozambique. In December 2006, Sasol started up its 34,000 bpd Oryx gas-to-liquid (GTL) facility in Qatar and today this facility produces more than its design capacity. The world's largest GtL facility was built by Shell in collaboration with Qatar Petroleum. It has a capacity of 140,000 bpd and it has been fully operational since 2012. The facility was completed at a final cost of about $19 b (Platts, 2013). These examples illustrate the current commercial scale of this technology and the high capital costs required to construct a facility based on "easier" feedstocks (natural gas and coal).

A biomass-to-liquids process is expected to pose greater challenges based on a more heterogeneous biomass feedstock, production of a lower quality syngas, the smaller scale and feedstock availability risks (Hileman et al. 2009).

3.10 TECHNO-ECONOMIC CONSIDERATIONS OF GASIFICATION BASED BIOFUELS

The cost of gasification-derived biofuels can be estimated quite accurately since the processes are based on established industrial processes in the coal gasification industry. A techno-economic study by ISU/ConocoPhillips/NREL (Swanson et al., 2010) estimated the cost of gasoline produced from FT conversion of biomass syngas. The study assumed a corn stover cost of $83/odt, a 2000 tpd facility and a 10% ROI and compared two scenarios of: a) low temperature using a fluidised bed gasifier at 870 °C, and b) high temperature using an entrained flow gasifier at 1300 °C. Both scenarios were followed by Fischer-Tropsch synthesis and hydroprocessing of the resulting FT liquids. Some of the results for both the high temperature (FTHT) and the low temperature (FTLT) scenarios are summarised in Swanson et al. (2010). Although the FTHT scenario had 20% higher capital costs, its minimum fuel selling price (MFSP) was about 10% lower. This was achieved because of the much higher conversion efficiency of the high temperature approach. The highest sensitivities of the FTHT scenario are mainly the capital costs, feedstock costs and compressor capacity. A 30% increase in capital costs resulted in an 18% increase in MFSP. An increase in the feedstock cost from 75 to $100/odt, resulted in a MFSP of 10% increase. An increase in the compressor install factor from 1.2 to 3 further increased the MFSP by 17% (Swanson et al., 2010).

Table 15 Techno-economic studies on gasification-derived biofuels

(Plant size: 2000 tpd of dry basis biomass, cost basis year: 2007)

	2010 NREL (FTHT)	2010 NREL (FTLT)
Facility fuel output (MGPY)	39.8	32.3
(MLPY)	(150)	(122)
Fuel yield (gasoline gallon Equivalents/metric tonne)	61	47.2
(gasoline L Equivalents/metric tonne)	(231)	(179)
Total Project Investment (TPI, million $)	606	498
(equipment only, million $)	(309)	(254)
TPI for Gasifier (million $)	68	28
TPI for Syngas cleanup & conditioning	34	29
TPI fuel synthesis	49	59
TPI Hydroprocessing	33	30
TPI Power generation	46	39
Transportation fuel MFSP (Minimum Fuel Selling Price ($/gal)	4.27	4.83
($/L)	(1.13)	(1.28)
($/GJ)	(31.4)	(35.5)
MFSP Feedstock	28.9%	32.9%
MFSP Capital Depreciation	14.8%	13.9%
Feedstock cost ($/MT)	75	75

Source: (Swanson et al., 2010)

Overall, the estimated MFSP and capital costs for both low and high temperature scenarios are high and they range between $4.3 and $4.8/gal ($1.1-1.3/L or $31-36/GJ), and between $500 and $600 (TPI) million respectively. These costs represent mature facilities while pioneer facilities were estimated to have about twice the TPI capital cost ($1400 million for the high temperature scenario and 830 million for the low temperature scenario). These costs are double the values estimated for pyrolysis, as discussed earlier. However, a direct comparison is difficult to make, both because of the known disparities in assumptions and costing of these types of analyses and also because of technological maturity differences. Despite its

high apparent cost, the gasification platform can be viewed as being more technologically mature than pyrolysis (especially when compared to the low maturity of pyrolysis oil upgrading technologies) and it has also leveraged know-how from industrial coal gasification. For example, the assumed catalyst lifespan in gasification is about 3 years, and it is more likely to be reached than the 1 year catalyst lifespan projected for pyrolysis oil upgrading as discussed earlier.

When the sensitivities of the pyrolysis and gasification analyses are compared, the biggest sensitivities for pyrolysis relate to yields, catalysts and hydrogen costs while for gasification they are the capital expenditure and the feedstock costs. Compared to pyrolysis, gasification is a high capital expense platform due to the higher operating temperatures that are needed, the complexity of the process, the multiple process steps and the requirement for various heat-cool and compression cycles. As gas compressors are very energy and capital-intensive the compressors accounted for about 18% of total equipment costs. The compressor capacity of a gasification facility is directly related to the process efficiency, thus the lower the *per pass* yield of a process, the more a compressor has to work to recycle the gas stream enough times until it has reacted fully.

When comparing gasification to pyrolysis facilities, hydroprocessing equipment (mainly used for cracking the heavy ends of FT liquids) usually represents a lower proportion of overall capital costs (see Table 15). The insertion of hydrogen into a gasification process contrasts with what was discussed earlier for pyrolysis. In gasification, unlike pyrolysis, there is usually minimal to no external hydrogen supply and the biomass syngas itself is the source of the energy and hydrogen needed to reduce and deoxygenate carbohydrates to drop-in biofuel hydrocarbons.

Brown and Wright (2014) analyzed the economic feasibility of eight different pathways of biofuel production under price uncertainties. Two scenarios were simulated based on Swanson et al. (2010) and updated. The results, instead of showing a MFSP, presents a maen 20-year NPVs with a wide standard distribution. NPVs of FTHT and FTLT were calculated respectively of -$455 M and -$493 M based on 2013 Annual Energy Outlook. Both scenarios had zero probability of a positive NPVs which showed the production cost over the product's future marketing value.

As the capital cost showed the greatest sensitivity for the gasification platform, it is not surprising that large scale facilities are projected to reduce the high MFSP of gasification biofuels. It has been suggested that a 500 MW$_{th}$, facility, or one with 2000 tpd of feed or producing 3,200 bpd of gasoline equivalent

(GGE), is the minimum scale at which a biomass FT facility can be viable (Hayes, 2013). This would not be considered to be a large facility when compared to the currently operating fossil FT facilities of Sasol and Shell as indicated in Table 16, where the scale of facilities is compared.

Table 16 Scale of selected GtL and BtL facilities

Technology	Facility	Scale(bpd)
Biomass (Corn Stover) gasification (2000 tpd)	ISU/COP/NREL techno-economic analysis	3,200
Coal gasification	Sasol, Secunda, South Africa	160,000
GTL (gas to liquids)	Pearl GTL, Shell, Natural gas, Qatar	140,000

Source: Company websites and (Swanson et al. 2010)

What has been modelled to represent a full scale, biomass-to-biofuel facility is at least 50 times smaller than the current commercial Sasol CtL (coal to liquid) main gasification facility and even smaller than Shell's Pearl GtL (gas-to-liquids) facility. As noted, the scale of a biomass facility will likely be limited by its access to feedstock and thus a larger scale facility will be challenged to reach the scale of the fossil-based facilities which utilise denser and more transportable feedstocks.

Although gasification is generally viewed as a process requiring large scale facilities to be more economically attractive, some technology providers have recently advocated the construction of smaller plants. For example, the company Velocys has built small scale syngas-FT liquids platform based on a microchannel reactor design which can be applied to small scale biomass gasification platforms (as low as 1400 bpd). ENVIA Energy's gas-to-liquids plant in Oklahoma City, completed in 2016, using Velocys technology to produce renewable fuels from landfill gas and natural gas[83]. Velocys also provided the FT platform for Red Rock Biofuels, which was recently acquired by Joule Unlimited. They plan to build a 14-16 million gallon wood-to-biofuels (jet fuels and drop-in diesel) in Lakeview, Oregon[84].

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[83] http://www.velocys.com/our-biorefineries/
[84] https://globaljusticeecology.org/wp-content/uploads/Red-Rocks-media-briefing.pdf

3.11 THE IEA BIOENERGY TASK 33 AND TASK 39 DATABASES

For an extensive list of global demonstration and commercial gasification facilities, the reader is referred to IEA Bioenergy's Task 33 (Gasification) online database. This online tool (see Figure 19) features an interactive world map with the gasification facilities at demonstration or operation stage. According to this interactive map, most of the biomass gasification activities are concentrated in Germany, Austria and the Scandinavian countries. In conjunction with the gasification database, the Task 39 demonstration database specifically focuses on biofuel production facilities (http://demoplants.bioenergy2020.eu/).
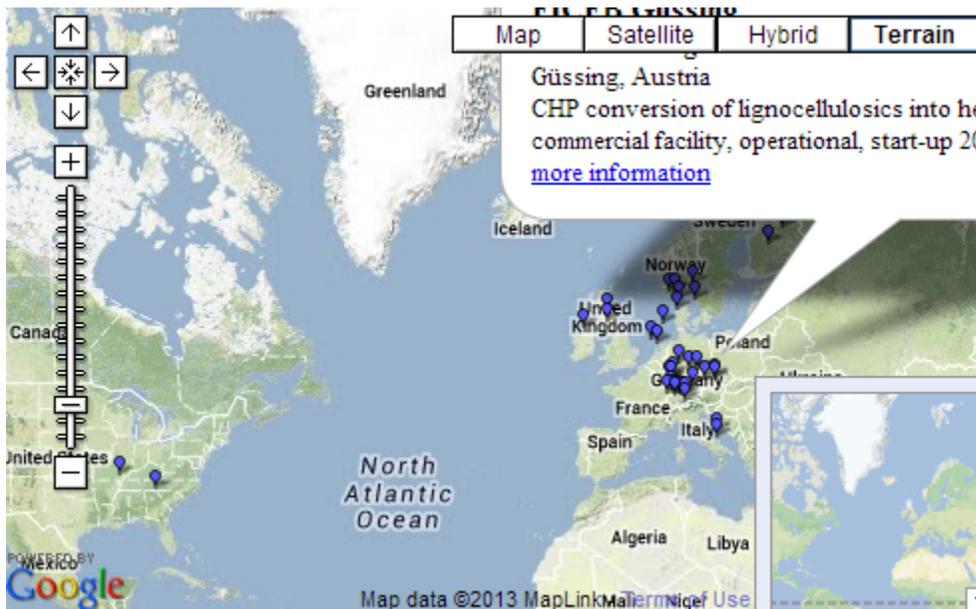

Figure 19 The IEA Bioenergy Task 33 gasification facility database

3.12 KEY CHALLENGES TO DROP-IN BIOFUEL PRODUCTION VIA THE GASIFICATION PLATFORM

The development of biomass gasification has progressed substantially over the last couple of decades as indicated by the more than 500 MW of operating biomass gasification CHP facilities around the world. The biogas-to-distillates end of the process also benefits from industrial "know-how" based on the operation of Sasol coal-to-liquids facilities. However, the upgrading of syngas to transport fuels remains a significant challenge, primarily due to high capital costs. These costs are due to the high temperature and high complexity of the gasification platforms which typically include various heat-cool and compression cycles. To try to mediate these high capital costs, it has been suggested that a minimum scale of 2000 tpd size facility will be needed. However, this can be considered to be relatively small scale when compared to current, commercial fossil based FT-distillates facilities which are at least 50 times larger. It can be anticipated that FT synthesis facilities which gasify biomass will be equally, if not more, challenging to operate at scale than are their fossil counterparts (CtL and GtL). However, a major advantage of gasification is that the perceived technology risk will likely be lower than that of the other biofuel platforms because, from a chemical standpoint, syngas is sufficiently similar to commercially upgraded fossil syngas. However, this perception can be challenged as biomass syngas is generally of inferior quality to coal-derived syngas and natural-gas-derived syngas in particular. For example, the tar content in biomass syngas (gasification and tar conversion technology dependent, up to thousands of ppm) is typically much higher than that seen in coal-derived syngas and orders of magnitude higher than can be accommodated in FT synthesis (about 5 ppm) to biofuels. Tar accumulation, capital costs and scale up challenges have been suggested to have been the main reasons behind the recent failure of the three commercial size start-up, biomass-to-distillates gasification facilities of NSE biofuels, Range Fuels and Choren [85, 86]. Techno-economic studies have shown that the manufactured selling price (MFSP) of gasification biofuels can be between \$31-\$36/GJ while the capital costs (TPI) required to build a pioneer commercial facility can be in the vicinity of \$1 billion for a drop-in gasification plant processing 2000 tpd of biomass (dry basis). However, not-with-standing these challenges, there is still significant potential for gasification technologies as new systems and technologies are developed.

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[85] https://www.biofuelsdigest.com/bdigest/2011/12/05/the-range-fuels-failure/
[86] http://www.etipbioenergy.eu/?option=com_content&view=article&id=277

From a systems point of view, the "hub and spoke" model of biomass logistics may provide an opportunity for a gasification facility to be built at a very large scale where pyrolysis will provide the densified biomass feed and oil refineries will be used for the last upgrading steps of the FTS process.

From a technology point of view, researchers and companies, (such as Velocys which claim efficient FTS of biomass at small scale (1400 bpd)) continue to make significant progress in all aspects of the process. For example, cleaning technology (e.g. KIT claiming production of "tar free" syngas from entrained flow gasifiers) and an increased interest in dimethyl-ether as an alternative fuel to diesel (e.g. the "BioDME" project in Europe) have already made an impact on the technical end economic feasibility of this approach to drop-in biofuel production (E4tech, 2009).

4. THE BIOCHEMICAL PLATFORM

Biomass conversion through biological means, such as by enzymatic hydrolysis followed by biological sugar conversion, has been termed the "biochemical" approach to producing drop-in biofuels. In the same way that glucose is fermented to ethanol for conventional (sometimes termed first generation) biofuel production, these "advanced" biocatalytic processes convert sugars to less oxygenated, more energy-dense molecules such as longer chain alcohols (butanol, butanediol) and higher molecular weight compounds such as isoprenoids and fatty acids. The earlier report, Karatzos et al. (2014) provides a detailed overview of various pathways in the biochemical platform and this will not be repeated in this update.

There are numerous biological pathways, feedstocks, and microorganisms that can be utilised for the production of drop-in biofuels and intermediates (Figure 20). Microorganisms such as cyanobacteria and algae can directly capture CO_2 from the atmosphere and convert it to ethanol or lipids. Alternatively, bacteria, yeasts and heterotrophic algae can utilise sugars derived from sugar cane, sugar beet, starch and other energy storage polysaccharides, or from the hydrolysis of the cellulose and hemicellulose carbohydrates in cellulosic biomass. Other bacteria can utilise hydrogen and carbon monoxide in syngas to produce alcohols, etc. The three main categories of intermediates that are produced include alcohols (ethanol and butanol), fatty acids (similar to lipids in vegetable oils) and longer hydrocarbons (such as isoprenoids, e.g. farnesene). These intermediates can all be used to make drop-in biofuel products through different routes. Isoprenoids can be upgraded into hydrocarbon fuels through a simple hydrotreating step. This is done by Amyris to produce farnesane as a biojet fuel, although only at low blends (10%). Fatty acids can be upgraded through the oleochemical pathway into drop-in biofuels as a jet or diesel replacement. Shorter molecules containing oxygen, such as ethanol and butanol, can be used to produce drop-in biofuels through the alcohol-to-jet pathway and this is further discussed under the hybrid platforms.

Cyanobacteria, yeasts and bacteria can be selected or engineered to produce either higher alcohols or isoprenoids and lipids and the metabolic pathways from one organism can be heterologously expressed in another. However, after biological production, regardless of which biosynthesis route is used, some form of hydroprocessing of the produced intermediate is typically required to saturate double bonds, etc.

before blending with conventional petroleum fuels. As described earlier, the more oxygenated and unsaturated the intermediate, the more hydrogen is required for it to be upgraded to a fungible drop-in functional equivalent to diesel, jet or gasoline blendstock.
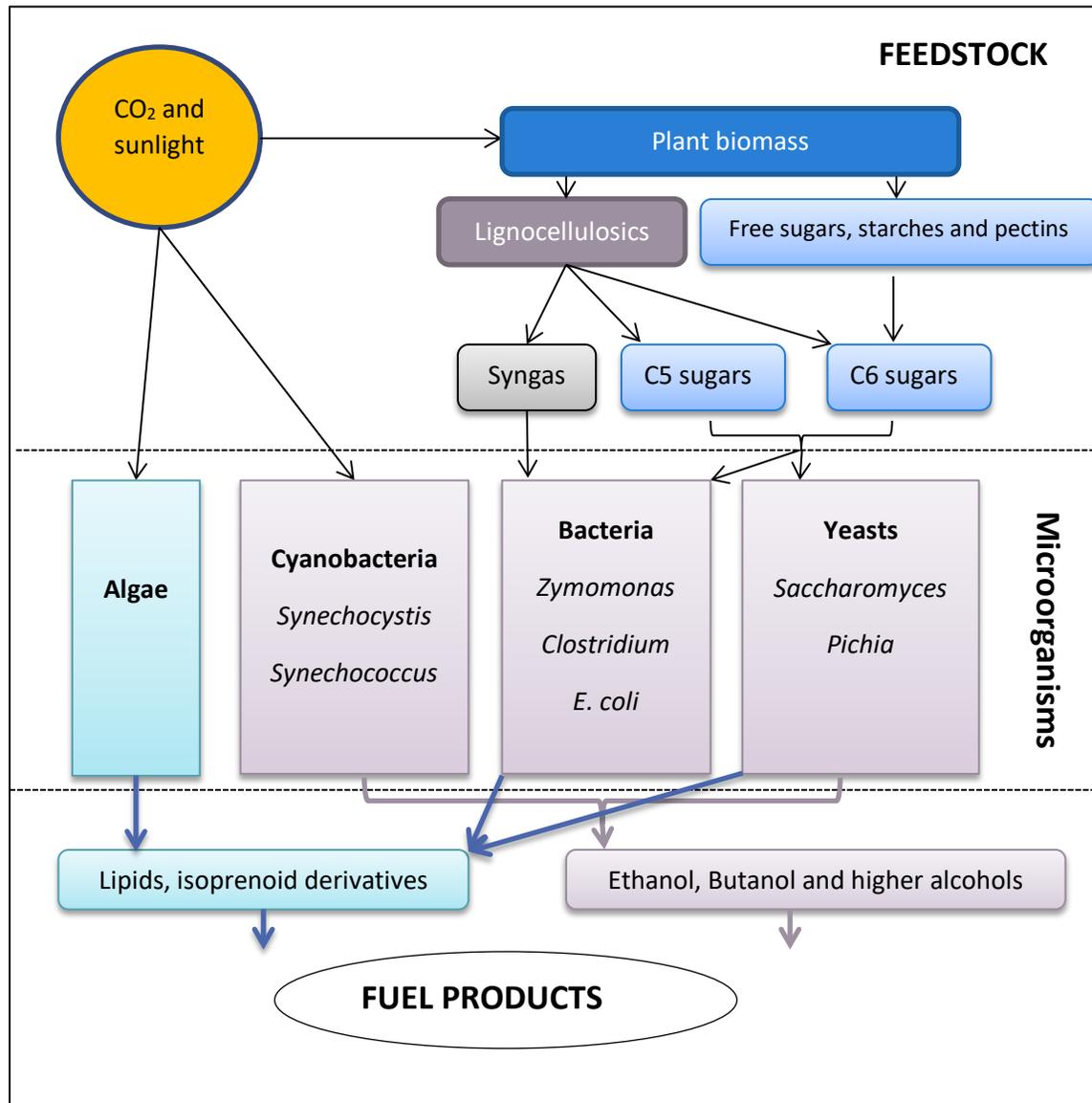

Figure 20 Schematic overview of the microorganism-to-drop-in-intermediate or biofuel derived for various renewable feedstocks. Source: adapted from (Weber et al. 2010)

From a commercialization point of view, one of the most attractive aspects of biochemical technologies is the potential to "piggy-back" onto existing ethanol facilities by switching the microorganism being used

in the microbe-to-ethanol process to obtain a "microbe-to-drop-in fuel or fuel intermediate" process. However, high process efficiencies must be achieved and the industrial robustness of the process at commercial scale must be proven.

In the earlier report (Karatzos et al, 2014) it was concluded that the production of higher value chemicals based on the biochemical platform was a more attractive value proposition than biofuels. However, some biochemical products can be used as biofuels, as chemical feedstocks or as solvents, with fuels generally the lowest value proposition. Unlike the thermochemical technology platforms that produce a mixture of hydrocarbons, the biochemical based platforms can produce single products at high selectivity. From an energy and hydrogen balance standpoint, biochemical platforms are more efficient at producing oxidized products than highly reduced molecules.

The use of these products as chemical feedstocks for applications like bioplastics production tends to be more profitable than as fuels. Several of the advanced biological conversion companies (e.g., Amyris, Gevo) are currently generating a significant part of their revenue from sales of biobased products rather than drop-in biofuels. Other companies have clearly stated they are primarily targeting value added oxygenated products such as dicarboxylic acids (e.g., Myriant's biosuccinic acid[87]) and dialcohols (e.g., Genomatica's 1,4 butanediol[88] or DuPont Tae and Lyle's 1,3-Propanediol[89]). It is probable that the initial focus on biofuels was perhaps due to the greater availability of financing and funding opportunities to assist companies in commercialisation.

The Biotechnology Innovation Organization expects that by 2020 biobased products will make up 11 percent of the $3,401 billion global chemical market and sales will reach $375-$441 billion[90]. The value-added chemicals bio-based chemical markets are growing rapidly and this is expected to continue to expand for the foreseeable future, driven by a growing awareness of the benefits of being able to market renewably sourced products.

As stated earlier, it is unlikely that most biochemical drop-in production will be used as fuels before their higher value markets as chemicals are saturated. With fewer processing steps and less hydrogen consumption and higher feedstock conversion yields, biochemical platform technologies can be used to

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[87] https://www.gcinnovationamerica.com/biochemicals-bioplastics
[88] https://www.genomatica.com/products/
[89] http://www.duponttateandlyle.com/our_process
[90] https://www.bio.org/advancing-biobased-economy-renewable-chemical-biorefinery-commercialization-progress-and-market

produce oxygenated and low H_{eff}/C products that will likely generate higher revenues as higher value chemicals than as biofuels. Market saturation issues for renewable chemical products should not be too much of a concern in the near term due to projected strong growth in bio-based material markets.

One exception in this trend has been in the production of biojet fuels. Gevo obtained ASTM certification for their isobutanol to jet technology in 2017 while Lanzatech obtained ASTM certification for their ethanol to jet technology in 2018. It appears that the high demand for biojet fuels and their limited commercial availability has driven development of these pathways, even where these biojet fuels came at a premium cost. Gevo's isobutanol-based biojet was used in biojet flights from Chicago's O'Hare airport on Fly-Green Day in November 2017 while Lanzatech's biojet was used by Virgin airlines recently[91].

4.1   BIOLOGICAL PRODUCTION OF DROP-IN BIOFUELS

There are four main metabolic pathways that have been proposed for the conversion of glucose to the chemically reduced molecules that could constitute drop-in biofuels. The four pathways are shown in Figure 21 and they all begin with the oxidation of glucose to two pyruvate molecules (glycolysis). From there the pathways differ as the pyruvate is converted to various intermediates such as Acetyl CoA or acetaldehyde. The pathways that lead to butanol and alcohol are anaerobic whereas the pathways that lead to more saturated longer chain molecules such as isoprenoids or fatty acids are aerobic (Jin et al. 2011). Each pathway plays a different role in the production of drop-in biofuels in terms of productivity and suitability for drop-in biofuel production.

```
                    ┌──────────┐
                    │ Glucose  │
                    └──────────┘
                         │
                         ▼
┌─────────────────┐  ┌──────────┐          - O₂ reduction
│ Pyrophosphate   │  │ Pyruvate │───────────────────┐
│ intermediates   │◄─│          │                   │
│ DMAPP, IPP      │  └──────────┘                   │
└─────────────────┘  1 (aerobic)                    │
        │                │                          │
        │           + O₂ decarboxylation            │
        │                ▼                          │
        │           ┌───────────┐                   │
        │           │ Acetyl CoA│                    │
        │           └───────────┘                   │
        ▼           ╱          ╲                     ▼
┌──────────────┐ ┌───────────────┐          ┌──────────────┐
│ Isopropenol  │ │ Acetoacetyl-CoA│         │ Acetaldehyde │
└──────────────┘ └───────────────┘          └──────────────┘
                  ╱            ╲                     │
         2 (anaerobic)    3 (aerobic)        4 (anaerobic)
              ▼                ▼                     ▼
        ┌──────────┐    ┌──────────┐         ┌──────────┐
        │ Butanol  │    │ Fatty    │         │ Ethanol  │
        └──────────┘    │ acid     │         └──────────┘
                        └──────────┘
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1. Isoprenoid pathway (aerobic)
2. ABE pathway (anaerobic)
3. Fatty acid pathway (aerobic)
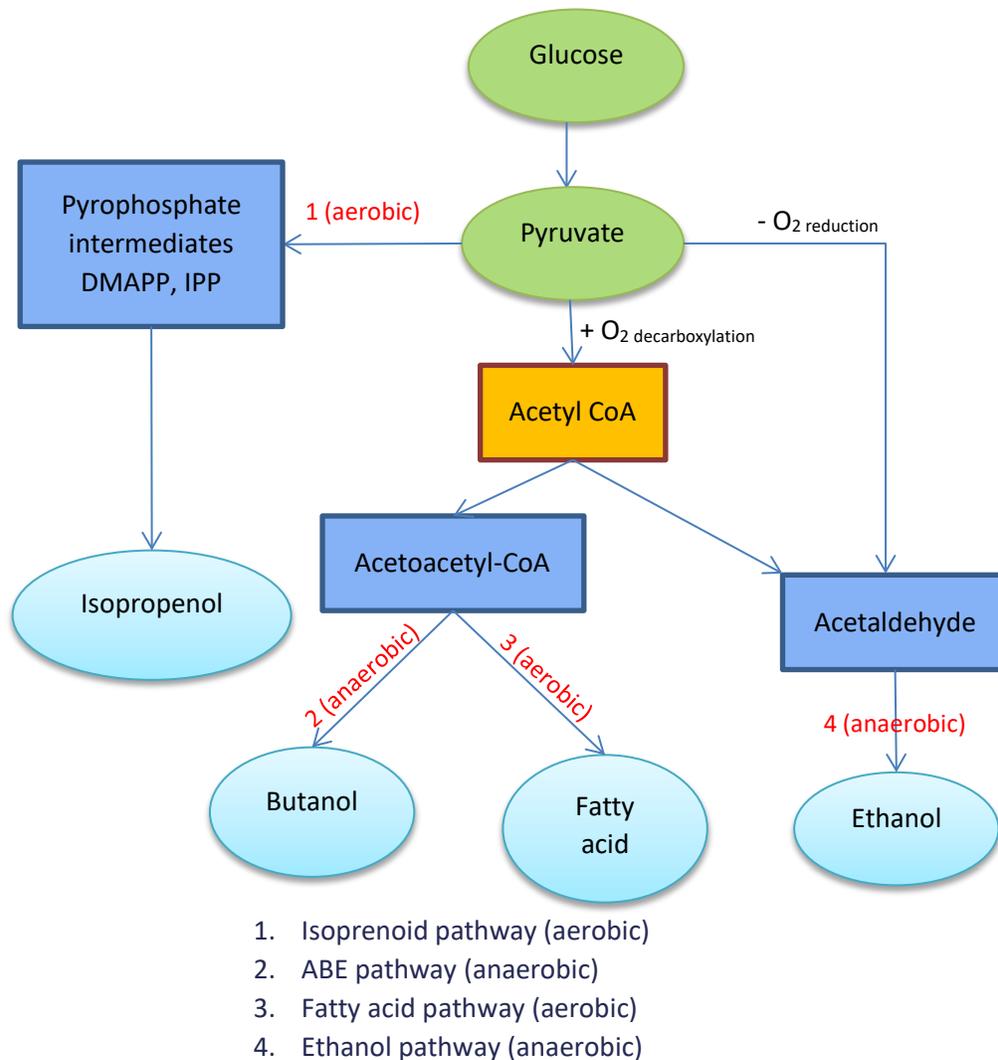4. Ethanol pathway (anaerobic)

Figure 21 Simplified schematic of major metabolic pathways relevant to drop-in biofuel production.

As these pathways have been described in greater technical detail previously (Karatzos et al, 2014) the material will not be repeated here.

In a related approach, IEA Bioenergy Task 39 published a comprehensive report on the potential of using algae for biofuel production in 2010[92]. This was followed by an updated report in 2017 State of Technology review[93] and a short summary published in Algal Research[94]. The most recent report concluded that,

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[92] http://task39.sites.olt.ubc.ca/files/2013/05/IEA-Task-39-Current-Status-and-Potential-of-Algal-biofuels0.pdf

[93] http://www.ieabioenergy.com/publications/state-of-technology-review-algae-bioenergy/

[94] http://www.ieabioenergy.com/wp-content/uploads/2013/09/Laurens-2017-Renewable-energy-from-algae-perspective.pdf

although substantial technical progress has been made in developing algae-based bioenergy/biofuels, most projects have moved away from a strategy solely focused on biofuels to a multi-product biorefinery approach that can produce higher-value bioproducts for additional revenue to improve the economics.

One aspect of industrial scale up of biochemical pathways is the opportunity to leverage existing oil refinery infrastructure. In the case of biological production processes, the only step that can readily be performed at a petroleum refinery is the final hydrotreatment step, if needed, as well as perhaps final blending to create a fungible blendstock. As long as the oxygen content of biologically produced intermediates can be brought to roughly the same level as vegetable oils or fatty acids (~10 wt%), they can be treated in a similar way as oleochemical feedstocks, as discussed earlier.

4.2 EXAMPLES OF COMPANIES OPERATING ON A BIOCHEMICAL PLATFORM FOR PRODUCTION OF HIGHER ALCOHOLS AND DROP-IN BIOFUELS

Although a number of companies have been trying to commercialise the biochemical technology route to drop-in biofuels, several of these companies have diverted their focus to the more lucrative biochemical markets. For example, LS9 was bought by REG in 2015 and became their Life Sciences Division. Solazyme, using algae as a platform, changed their name to TerraVia and then declared bankruptcy in August 2017[95]. Sapphire Energy and Joule Unlimited have also run into difficulties.

Gevo, based in Colorado, USA, has a patented Gevo Integrated Fermentation Technology (GIFT) approach to isobutanol production[96]. Unlike n-butanol, isobutanol is branched and thus has better cold-flow properties. The GIFT process consists of genetically engineered yeast and continuous *in situ* recovery tailored to isobutanol extraction from fermentation broth. Although details are not publically disclosed, based on publically available presentations and patents (Evanko et al. 2012), the preferred recovery route is likely to be gas stripping because isobutanol has a boiling point of 108 °C compared to n-butanol's boiling point of 118°C. This attribute in itself possibly makes the recovery less energy intensive. The exact productivity of the GIFT platform is not publically known although in consultancy reports Gevo has claimed 5 times higher productivity than reported to date for n-butanol (Nexant 2012). Gevo has a strategic collaboration with ICM, the engineering company that has designed 60% of the US's existing corn to

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[95] http://www.biofuelsdigest.com/bdigest/2017/04/19/terravia-in-the-wilderness-years/
[96] http://www.gevo.com/

ethanol mills. The first 3.8 MLPY (1 MGPY) demonstration facility was "bolted on" to a corn to ethanol facility in St Joseph, Missouri. In September 2010, Gevo acquired its first production facility in Luverne, Minnesota and commercial production of biobased isobutanol and ethanol has been ongoing since 2014. The isobutanol that is produced at the facility is either sold directly or upgraded at a biorefinery in Silsbee, Texas (Gevo collaborate with South Hampton Resources Inc.) to jet fuel or isooctane (gasoline)[97]. Other strategic partnerships Gevo is pursuing include the Coca-Cola Company, Toray Industries Inc. and Total SA.

In August, 2015, Gevo and Butamax ended a patent lawsuit and agreed to worldwide patent cross-licences and settlement agreements. Under the new agreement, Butamax has taken the lead in developing on-road gasoline blendstock while Gevo focused on biojet fuel production[98]. Gevo obtained ASTM D7566 certification for their isobutanol-to-jet fuel product in 2016 and Alaska Air used Gevo's ATJ-SPK in a commercial flight[99]. While Gevo and Butamax both target isobutanol, other biobutanol start-ups are focused on "conventional" n-butanol produced via the traditional ABE pathway.

More recently the biomass to cellulosic sugar conversion technology developer Renmatix Inc., announced a Joint Development Agreement (JDA) with Gevo to evaluate the commercial feasibility of creating renewable jet fuel by integrating Renmatix's Plantrose Process with Gevo's GIFT™ technology and alcohol-to-jet (AtJ) process[100].

Another high profile company who has been looking at the biochemical route to drop in biofuels is Amyris. Amyris is a University of California, Berkeley spin off company founded in the San Francisco Bay area in California, USA in 2003. In 2005, the company received a grant from the Bill and Melinda Gates Foundation to optimize a yeast-based isoprenoid biosynthetic platform for producing the antimalarial drug precursor artemisinic acid[101]. Using this same synthetic biology platform Amyris later collaborated with the French oil company Total to commercialize production of farnesene as a diesel and jet drop-in biofuel component. Farnesene, marketed by Amyris under the trade name Biofene™, is also used as a precursor for cosmetic

[97] https://gevo.com/wp-content/uploads/2018/02/isobutanol-process.pdf
[98] http://ir.gevo.com/phoenix.zhtml?c=238618&p=irol-newsArticle&ID=2081456
[99] http://www.biofuelsdigest.com/bdigest/2016/03/28/gevos-alcohol-to-jet-fuel-clears-key-astm-hurdle/
[100] https://globenewswire.com/news-release/2018/12/06/1663130/0/en/Renmatix-and-Gevo-Sign-a-Joint-Development-Agreement-to-Evaluate-the-Commercial-Feasibility-of-Creating-Cellulosic-Hydrocarbons-for-Global-Renewable-Jet-Fuel-and-Gasoline-Markets.html
[101] https://www.berkeley.edu/news/media/releases/2004/12/13_gates.shtml

ingredients such as squalene which is normally extracted from the fat of large sea mammals. The saturated alkane, farnesane received ASTM certification to be used as a jet fuel in 10% blends with fossil jet fuel (synthesized isoparaffins SIP-SPK).

The company had a production plant located in Brotas, San Paulo, Brazil with an up to 40 million litre of farnesene capacity. Royal DSM completed the purchase of the Amyris' Brotas I fermentation facility in December 2017 and took over the construction of Brotas II, which will focus on "an expanding number of high-value, specialty ingredients"[102]. In other areas, Amyris and Chevron are working together to bring renewable base oils (lubricants) to automotive, industrial, marine and construction markets. More recently, Chevron, announced an equity investment in Novvi, a joint venture between Amyris and Cosan[103].

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[102] https://www.bioplasticsmagazine.com/en/news/meldungen/20180102-A-done-deal--DSM-completes-purchase-of-Amyris-Brotas-1-fermentation-facility.php
[103] http://www.biofuelsdigest.com/bdigest/2018/07/11/amyris-same-as-it-never-was/

5. HYBRID PLATFORMS

Although the majority of drop-in biofuel technologies are captured under one of the previously described oleochemical, thermochemical or biochemical platforms, some technologies combine approaches from two or more platforms and are thus categorised as "hybrid" routes to drop-in biofuels. The main examples include:

- Biological conversion (fermentation) of biomass gasification-derived syngas to alcohols. The main company in this space is Lanzatech.
- The thermochemical catalytic conversion of sugars and perhaps other solubilized carbon species to hydrocarbon biofuels. Virent Energy Systems ("Virent") is the primary current developer trying to commercialize this approach.
- The thermochemical catalytic conversion of biochemical platform produced alcohols (e.g., ethanol or butanol) to hydrocarbon biofuels. Gevo is pursuing this approach.

Each of these hybrid technologies offer advantages as well as present new challenges compared to thermochemical or biochemical platform routes discussed earlier. For example, traditional sugar fermentation is able to ferment only the saccharide portion of biomass whereas syngas can be produced from the entire biomass carbon (i.e., including lignins, extractives and other non-sugar carbon-containing compounds) such that there is potential to convert more of the feedstock to fuel product(s) via syngas fermentation. Similarly, catalytic conversion of sugars and other organic carbon compounds offers the potential to convert sugars and perhaps more than just sugars to a broader range of higher energy products than available via traditional biological conversion technologies. The third approach, alcohol-to-drop-in, involves the catalytic conversion of higher H_{eff}/C alcohols rather than lower H_{eff}/C sugars (for which $H_{eff}/C = 0$) but is otherwise conceptually similar to catalytic upgrading of sugars. These three hybrid routes to drop-in biofuels or fuel blendstocks are discussed further in the following sections.

Each hybrid platform has unique advantages such as fuller utilization of feedstock carbon in syngas fermentations, shorter reaction times in sugar catalytic upgrading or lower technical risk in alcohol-to-jet technologies. However, each approach also has significant challenges to overcome before they can reach full commercial scale. The high demand for biojet fuels and their limited availability is playing a major role in driving the commercialisation of the alcohol to jet pathways, particularly as ASTM certification was

obtained for both isobutanol and ethanol to jet processes. It is not clear how competitive these biojet fuels will be once other biojet fuels become more widely available.

5.1 LANZATECH AND SYNGAS FERMENTATION

As described earlier in the section on gasification, the conversion of syngas to liquid biofuels can be achieved thermo-catalytically. However, some fermentative microorganisms can also utilise syngas as their carbon and energy source while producing potential drop-in biofuel intermediates as a major product. Some autotrophic microorganisms can use single carbon compounds such as CO and CO_2 as sources of carbon and energy-rich compounds such as CO and H_2 as sources of energy. In the same way thermochemical syngas upgrading involves the use of catalysts, microorganisms that convert syngas to biofuels such as ethanol require metals such as cobalt and nickel (in relatively trace amounts) to catalyze essential metabolic enzyme activities (Hayes 2013). A range of microorganisms can ferment syngas to intermediates such as ethanol, butanol and acetic acid, including acetogenic bacteria such as *Clostridium ljungdahlii* and *Clostridium carboxidivorans* (Munasinghe & Khanal, 2010)*.* These microorganisms use the *Wood-Ljungdahl* pathway to reduce CO to Acetyl-CoA, from which ethanol and butanol are produced via the pathways described in Chapter 4. The reducing power required for the first reaction comes from the H_2 in the syngas or from the oxidation of CO to CO_2 via a carbon monoxide dehydrogenase enzyme (Daniell et al. 2012; Weber et al. 2010). Here again, as seen in thermochemical deoxygenation routes discussed in Chapter 3, there is a trade-off between carbon efficiency and hydrogen consumption. From an evolutionary perspective these metabolic pathways are found in some of the most primitive microorganisms on earth. Approximately 4 billion years ago, well before oxygen became abundant in the atmosphere, these types of microorganisms survived by metabolising CO and H_2 gases (Daniell et al. 2012).

Syngas fermentation is claimed to have several advantages compared to its "parent" processes, i.e., sugar fermentation and thermocatalytic syngas conversion (Munasinghe and Khanal 2010; Daniell et al. 2012). For example, compared to sugar fermentation, this approach is able to utilise lignin in addition to carbohydrate fractions of biomass. In comparison to thermocatalytic syngas conversion it has also been claimed to be economical at a smaller scale, because of lower capital costs, while proving to be less sensitive to impurities (Daniell et al. 2012). However, the volumetric productivity of this hybrid approach is still quite low at around 0.3 g/L/h, similar to the biochemical production of butanol and farnesene. The primary limiting step for syngas fermentation is the low solubility of CO and H_2 gases in aqueous solutions

as these gases must first be absorbed into the aqueous fermentation broth to be microbially assimilated (Bredwell et al., 1999). As the gas-liquid mass transfer and solubility of both molecular hydrogen and carbon monoxide in water are quite low compared to more conventional sugar substrates (where gas-liquid mass transfer isn't needed), syngas fermentation rates are typically constrained by physical mass transfer limitations rather than being limited by metabolic capacities. From an energy balance perspective, syngas also has to be cooled down from a production temperature of ca. 700 °C or higher to ca. 50 °C or less before it can be fermented. This significant cooling requirement is of concern because large temperature fluctuations in gasification systems result in significant engineering challenges and generally have an adverse effect on process energy efficiency.

The gas-liquid mass transfer challenge of syngas fermentation platforms has been a long-standing focus of engineering research and various reactor designs have been assessed to try to improve the contact surface area between gases and liquids and achieve increased dissolution and diffusion rates. Designs include continuous stirred tank, microbubble dispersion stirred tank, bubble or gas lift columns, hollow fiber and other membrane-based systems, trickle bed and monolithic biofilm reactors. A detailed description of possible reactor designs and their operation and relative efficiencies has been provided by Munasinghe & Khanal (2010).

Founded in New Zealand in 2005, and headquartered in Chicago, Illinois, LanzaTech has developed a gas-substrate fermentation process to produce ethanol and other and chemicals from carbonaceous CO-rich gases. LanzaTech operates research laboratories in the USA, China and New Zealand, and currently operates multiple different scale facilities[104]. Their pilot facility, located at the BlueScope Steel mill in New Zealand and linked directly to the mill's off-gas exhaust, had been operating since 2008 (shut down currently) and has an ethanol production capacity of 15,000 gal/year (56,800 L/year). In November 2012, LanzaTech completed the first phase of a multi-phase project with Baosteel, China's largest steel producer. This demonstration facility has an ethanol production capacity of 100,000 gal /year (380,000 L/year) and could convert CO-rich waste gas from Baosteel's production facility using LanzaTech's gas fermentation technology. The second Steel demo plant was built in Caofeidian, China in partnership with the Shougang Group in 2012. LanzaTech also operates a commercial facility in Soperton, Georgia, USA

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named the Freedom Pines Biorefinery and two other pilot plants in Taiwan and Japan. The company has a number of high profile partners including the Shougang Group, Aemetis, Sekisui, and Baosteel etc., on the production side and Virgin Atlantic and Boeing on the product off-take side. For its aviation fuel projects, LanzaTech has partnered with the Pacific Northwest National Laboratory (PNNL) as they have worked on alcohol-to-jet catalytic conversion technology.

Syngas fermentation companies have shown ethanol can be commercially produced from CO and H_2-rich gases (syngas) or CO-rich gases via fermentation. Although ethanol is itself not a drop-in biofuel, at the right price point, it could be a viable intermediate for drop-in fuel production. However, the same fermentative pathways that are used for gas-based ethanol production can be used to produce even more reduced products and alcohols such as butanol are better suited than ethanol as drop-in biofuel intermediates.

Another company that operated in this space, INEOS Bio's technology was based on a patented process using proprietary microorganisms to convert biomass derived syngas to ethanol and other bio chemicals. However, the company experienced difficulties early on with hydrogen cyanide which was formed in the syngas and was toxic to the microorganisms. Although the company installed an HCN scrubber to clean up the syngas[105], the company decided to sell off its ethanol business in 2016[106].

5.2 AQUEOUS PHASE REFORMING AND THE VIRENT PROCESS

The technology for catalytically converting sugars or polyol feedstocks to monooxygenates, also known as aqueous phase reforming (or APR), is being developed by the company Virent Energy Systems (Virent). In 2016, the company was purchased by Tesoro. Using patented catalytic chemistry, Virent converts soluble biomass-derived sugars into products molecularly identical to those made with petroleum, including gasoline, diesel, jet fuel, and chemicals used for plastics and fibers[107].

This technology is classified as a hybrid platform because it converts sugars, nominally a biochemical platform feedstock, to drop-in biofuels using a thermochemical catalytic process. Variations of APR have

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[105] http://www.biofuelsdigest.com/bdigest/2014/09/05/on-the-mend-why-ineos-bio-isnt-reporting-much-ethanol-production/
[106] http://www.ethanolproducer.com/articles/13678/ineos-bio-to-sell-ethanol-business-including-vero-beach-plant
[107] http://www.virent.com/company/

also been used to produce hydrogen from the aqueous residues of pyrolysis oil separation and upgrading processes (Bridgwater, 2012). The APR technology builds on the pioneering work of researchers at the University of Wisconsin who showed that highly reduced carbon molecules could be produced when sugars (or other polyols) in aqueous solution were mixed with molecular hydrogen and passed over ZSM-5 catalysts (Huber and Dumesic 2006; Cortright et al. 2002; Huber et al. 2004). This initial work ultimately lead to the creation of Virent and the development of its patented BioForming™ process, which comprises a combination of the original APR process combined with upgrading technologies used in oil refineries, as further refined by Virent. In overview, this process employs heterogeneous catalysts operating at moderate temperatures (175 to 300 °C) and pressures (10 to 90 bar) and reduces the oxygen content of the (plant biomass derived) sugar or polyol feedstock through the three main steps described below (Blommel and Cortright 2008; Hayes 2013; Huber and Dumesic 2006):

a) Acid-catalyzed dehydration of sugars;

b) Aldol condensation of dehydrated carbohydrates over solid base catalysts to form large organic molecules;

c) Dehydration/dehydrogenation of the large organic molecules to alkanes using bifunctional catalysts (this step represents a variation of conventional catalytic processing as found in petroleum refineries)

A schematic representation of the process is shown in Figure 22.

The Virent process yields a product exhibiting similar properties to petroleum reformate, although the exact mixture composition depends on the nature of the catalysts and reaction conditions used. Acidic catalysts such aluminosilicates (e.g., ZSM-5) favour the production of shorter molecules of more phenolic nature (more suitable for gasoline blends) while base catalysts favour chain elongation through aldol condensation and thus form longer chain liquid products (more suitable for diesel blends) (Blommel and Cortright, 2008). Nobel metal catalysts such as Pt and Rh favour reforming of carbohydrates to hydrogen and CO_2 (Bauldreay et al. 2010).The reformate can then be upgraded to a drop-in biofuel using conventional refinery processes. The process consumes 12 wt% (of dry feedstock) hydrogen, some of which is produced via the APR process itself, as shown in Figure 22. Virent claims that >90% of the lower heating value (LHV) in the sugar and the hydrogen inputs is recovered in deoxygenated hydrocarbon products.

In 2016, Virent was acquired by Tesoro. And it formed a strategic consortium with Coca-Cola, Toray, Johnson Matthey to develop a commercial production for fuels and chemicals[108].
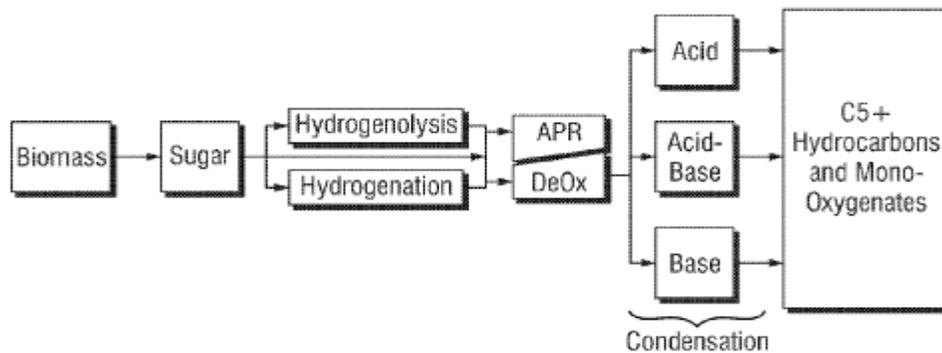
a)
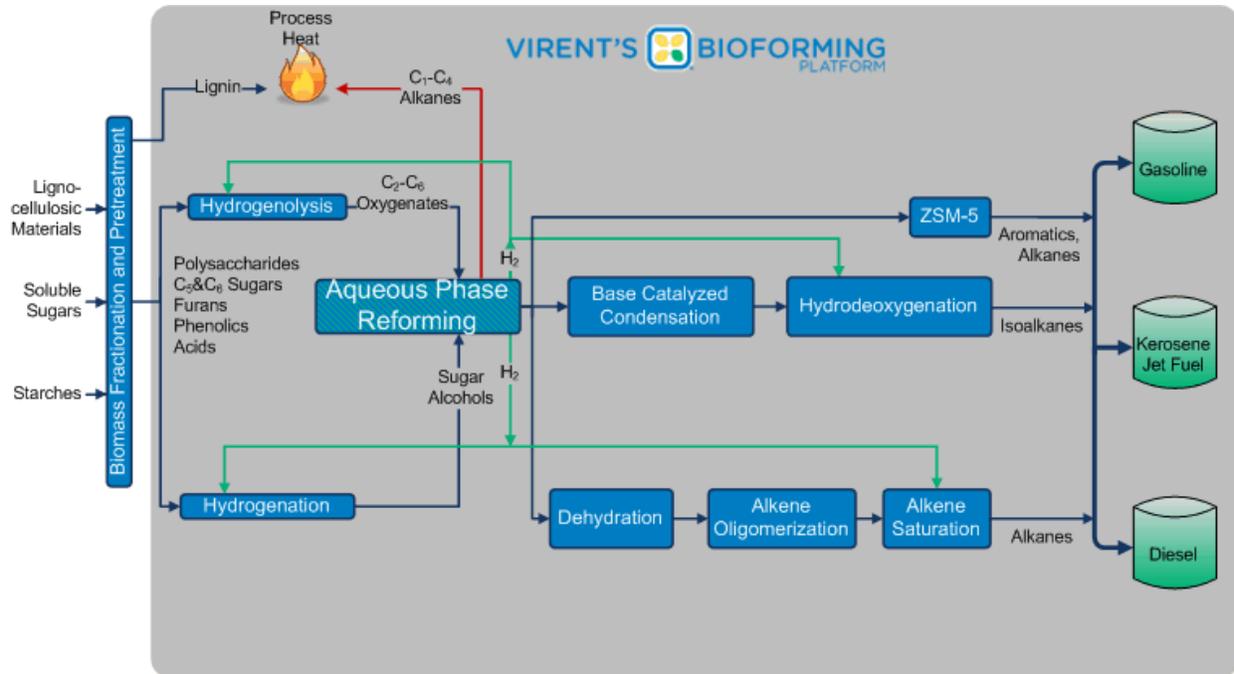
b)

Figure 22 The Virent process. (a) Entire process. (b) simplified representation emphasizing key steps.

Source: (Blommel and Cortright 2008; Bauldreay et al. 2010)

Compared to fermentation, the APR approach is attractive because it has the potential to be used to produce highly reduced (high H_{eff}/C) hydrocarbons from a diversity of water-soluble organic carbon compounds including both C5 and C6 carbohydrates and at much faster reaction rates than are possible

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"Drop-in biofuels: The key role that co-processing will likely play in its production"
IEA Bioenergy Task 39

using biochemical routes (e.g., residence times of minutes vs hours or days). However, the APR reactions are less selective than fermentation processes and produce a complex mixture of organic molecules. Although the APR process uses non-exotic process components and catalysts, it faces similar catalyst coking and deactivation challenges to those previously discussed in chapter 3 for pyrolysis oil upgrading. During catalytic upgrading of water-soluble saccharides and bio-oil fractions, catalyst coking and deactivation have been shown to increase with decreasing feedstock H_{eff}/C ratio. Feedstocks with an H_{eff}/C effective ratio less than 0.15 have been shown to cause large amounts of coke formation (more than 12 wt%) from homogeneous decomposition reactions Zhang et al. (2011). Given that sugars have an H_{eff}/C effective ratio of 0, demonstrating the ability to avoid coking problems through effective catalyst regeneration schemes will be key to commercializing aqueous phase reforming technology.

5.3 THE ALCOHOL TO JET PROCESS (ATJ)

The alcohol-to-jet (ATJ) process converts ethanol or other alcohols such as butanol to hydrocarbon mixtures which can be used as drop-in biofuels intermediates or blendstocks. The ATJ process is relatively simple, resembling the methanol to gasoline process discussed previously in the syngas upgrading section. The main processes involve dehydration, oligomerization and hydrogenation. The technology risk is low and the main challenge lies in the economics as it is an energy intensive process involving highly exothermic reactions. However, another challenge, as discussed for the oleochemical platform, is the final drop-in product might command a lower price than the feedstock alcohol.

Recent techno-economic analysis of the alcohol to jet process was carried out by Yao et al. (2017) which found that sugarcane was the lowest cost feedstock for jet production (via ethanol as an alcohol), followed by corn grain and switchgrass, with the mean breakeven jet fuel prices being $0.96/L ($3.65/gal), $1.01/L ($3.84/gal), and $1.38/L ($5.21/gal), respectively.

As mentioned earlier, ATJ based on Gevo's isobutanol conversion received ASTM D7566 approval for ATJ renewable jet fuel in 2016 and the ethanol to jet conversion received certification in 2018. This should further facilitate the commercialization of ATJ technologies. Large airline companies and the US Dept. of Defense have offered support to companies which produce jet fuels from alcohols. Gevo received support from Alaska Air which used some of its isobutanol to jet fuel product in two commercial flights[109]. Gevo's

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[109] https://globenewswire.com/news-release/2016/11/14/889663/0/en/Alaska-Airlines-to-Fly-Today-on-Gevo-s-Cellulosic-Renewable-Alcohol-to-Jet-Fuel.html

biojet fuel was also used on November 8, 2017 at Chicago's O'Hare airport as part of Fly Green Day with biojet fuel delivered via the airport hydrant system[110]. In October 2018, LanzaTech announced the first batch of biojet fuel was used on a commercial Boeing 747 from Orlando to London[111].

5.4   POWER TO LIQUIDS (PTL)

Power-to-Liquids is a platform that converts renewable electricity, water and CO_2 to liquid hydrocarbons[112]. Hydrogen is produced via water electrolysis using renewable electricity and liquid hydrocarbons can then be synthesized from H_2 and CO_2 to be further upgraded to drop-in fuels. The renewable CO_2 may be sourced from carbon capture technologies, directly from the air or from flue gases.

There are two major pathways for PTL, with similarities to syngas upgrading previously discussed under the Fischer-Tropsch (FT) pathway and the methanol pathway. In the FT process, contrary to gasification of biomass to get CO, the reverse water gas shift reaction is used to convert CO_2 and H_2 to CO and H_2O. Both of the processes are exothermic and produce waste heat for steam generation. We profile a number of companies operating in this space.

Sunfire, founded in 2010 in Bremen, Germany, develops and manufactures steam electrolysers (SOEC) and high-temperature fuel cells (SOFC). H_2 generated using SOEC can be converted to "Blue Crude" through a power to liquids process. SOEC is used for CHP based on the future concept of exact energy generation on heat and power demand. CO_2 can be partly extracted onsite from the ambient air by using the Direct Air Capture (DAC) technology developed by a Swiss company Climeworks. Three tons of "Blue Crude" was recently produced in its demonstration plant in Dresden, Germany, verifying continuous operation of 1,500 hours[113]. A first commercial plant that can produce 8,000 tons of Blue Crude and 20 MW electricity is planned to start operation in 2020 in Norway, which can supply up to 13,000 cars and reduce 21,000 tons of CO2 emissions from fossil fuel annually. The company also holds the exclusive rights

[110] http://biomassmagazine.com/articles/14818/on-fly-green-day-8-airlines-fly-with-gevoundefineds-jet-fuel-from-oundefinedhare

[111] http://www.lanzatech.com/virgin-atlantic-lanzatech-celebrate-revolutionary-sustainable-fuel-project-takes-flight/

[112] http://www.lbst.de/news/2016_docs/161005_uba_hintergrund_ptl_barrierrefrei.pdf

[113] http://www.sunfire.de/en/company/press/detail/first-commercial-plant-for-the-production-of-blue-crude-planned-in-norway

for Norway and Sweden since 2016 and plans to increase their capacity by tenfold after gaining enough experience from the first commercial plant.

Founded in 2006 in Reykjavik, Iceland, Carbon Recycling International (CRI) built the George Olah Plant in Iceland to produce methanol in late 2011[114]. In 2015, the capacity was expanded from 1.3 ML/Y to 5 ML/Y and can now recycle 5.5 thousand tonnes of CO_2 annually. Hydro and geothermal energy are used to supply electricity to the grid which is used by the plant to make H_2. The CO_2 is captured from flue gas by a geothermal power plant nearby. Methanol is produced by catalytic reaction between CO_2 and H_2 and the product is then sold to the market for blending with gasoline or as a chemical feedstock.

Founded in 2010, ANTECY is working on developing a technology that can convert solar and CO_2 from the atmosphere directly to liquid fuels and/or chemicals. CO_2 is plentiful around the world, however, clean and highly concentrated CO_2 is not commercially available. CO_2 concentration is very low in the air (around 400 ppm) for application in direct air capture and producing one ton of CO_2, 2,500 tons of air will be needed[115]. Flue gases contain higher concentrations of CO_2, however, other components are toxic and corrosive which make the clean-up difficult and expensive[116]. ANTECY developed CAIR that is based on a robust non-amine inorganic solid sorbent (K_2CO_3, $KHCO_3$) to capture CO_2 from air and/or flue gas. It eliminates the potential risk to the environment of toxic amine degradation and emission.

After CO_2 is obtained, several routes are proposed to produce methanol as a method of storage where it can be used in transportation or converted to a range of chemicals[116]. The most mature technology among different pathways is H_2 production by electrolysis, followed by thermo-catalytic conversion of H_2 and CO_2 to methanol. A less mature technology is developing an integrated platform of water splitting with CO_2 reduction. More research will be needed for photo catalytic conversion.

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[114] http://www.carbonrecycling.is/george-olah/
[115] http://www.biofuelsdigest.com/bdigest/2017/08/07/a-smart-faster-path-to-zero-lifecycle-emission-advances-from-the-eu-in-direct-carbon-capture-from-air/
[116] https://www.antecy.com/

Another potential Power-to-liquids company is Carbon Engineering which is located in Squamish, British Columbia, Canada. The company was found 2009, built a pilot plant to capture CO2 in 2015 and have been looking at the production of fuels since 2017[117]. As described on their website, the Direct Air Capture (DAP) technology involves four steps[118].

1. Air contractor. A strong hydroxide solution is used to capture CO2 into carbonate.
2. Pellet reactor. The carbonate solution is converted into small calcium carbonate pellets and dried.
3. Calciner. The pellets are heated in a circulating fluid bed and the CO2 released.
4. Slaker. The left calcium oxide from the calciner is hydrated and returned to the pellet reactor to regenerate the hydroxide capture solution.

After CO2 capture, the drop-in biofuels are produced via hydrogen production through water electrolysis, reverse water gas shift and syngas synthesis, as discussed previously.

[117] http://carbonengineering.com/company-profile/
[118] http://carbonengineering.com/about-dac/

6. CONCLUSIONS AND RECOMMENDATIONS

This report defines drop-in biofuels as "liquid bio-hydrocarbons that are functionally equivalent to petroleum fuels and are fully compatible with existing petroleum infrastructure". Although conventional biofuels such as ethanol and biodiesel have been produced and utilized at significant scales for many years, they are not fully compatible with existing combustion engines or the overall liquid transportation fuel refining and distribution network. Although a considerable amount of innovative work has been invested over the past several years, drop-in biofuels currently represent only a small percentage (around 2%) of global biofuel markets.

As described in the main body of the report and as summarised below, the predominant drop-in fuels that are produced today are made using the oleochemical/"conventional" platform to convert relatively highly reduced renewable lipid/oleochemical feedstocks such as vegetable oils, used cooking oils, tallow, and other lipids to fully saturated products. This technology is fully commercial and global production of hydrotreated vegetable oils has increased to about 5 billion litres production capacity. The oleochemical based processes exhibit high yields, require relatively low capital and hydrogen inputs (due to the use of relatively high H_{eff}/C feedstocks compared to lignocellulosic or sugar feedstocks) and are fully mature. This is the main source of drop-in biofuels used by the aviation sector. However, sourcing large quantities of "sustainable" feedstocks (lipids) at a low enough cost to result in profitable drop-in biofuel production remains challenging and is a major constraint limiting the expansion of this platform.

It is likely that thermochemical technologies based on more widely available feedstocks such as lignocellulose will provide the long-term supply of drop-in biofuels in the future. However, commercialisation of these technologies has been slow. Gasification combined with Fischer-Tropsch synthesis has produced commercial, finished fuels and this technology pathway was the first to receive ASTM D7566 certification as an alternative jet fuel in 2008, but based on drop-in fuels produced from these fossil feedstocks. Ongoing attempts to commercialise this technology based on biomass has proven problematic due to several reasons such as high initial investment costs, syngas cleanup and the large scale needed for economic viability challenging biomass feedstock logistics. In contrast, pyrolysis/hydrothermal liquid (HTL) can likely be carried out as at a smaller commercial scale. However the upgrading of biocrudes/ bio-oils into finished fuels has not yet been commercialised. Although a more stable bio-oil or biocrude with lower oxygen is highly desirable and easier to upgrade, similar infrastructure will likely still be required for cracking and hydroprocessing to upgrade any liquid

intermediate into finished fuels with strict specifications[119]. Upgrading liquid intermediates from any of the thermochemical liquefaction technologies through refinery integration using a co-processing strategy should be attractive in all cases. However, as detailed in the main body of the report, significantly more research is required to better understand the behaviour of biobased intermediates during co-processing and as well as the resulting economics of the different strategies.

Petroleum refineries versus drop-in biorefineries

Drop-in biofuel production generally proceeds in the two distinct phases of first, production of an intermediate, e.g. pyrolysis oil, followed by a second phase of upgrading the intermediate to a finished fuels. In the earlier report (Karatzos et al, 2014) an in-depth summary of the refining of crude oil through different refinery processing steps was provided, including distillation, cracking and hydroprocessing. Many of these processing steps are also used in upgrading intermediates into drop-in biofuels, although there are differences between crude oils and biological intermediate feedstocks. As noted in detail in the main report, some form of hydroprocessing is required for every type of technology pathway to make finished fuels, e.g. farnesene has to be converted into farnesane. For some biobased feedstocks, advanced processing such as catalytic cracking, isomerisation or fractionation is also required to make finished fuels to specifications. The predominant approach in development of drop-in biofuels has been dedicated upgrading of biobased feedstocks in biorefineries. This has been the basis of the oleochemical technology pathway with companies like Neste operating large biorefineries that hydrotreat fats and oil to produce biofuels. To date this is the only pathway that has produced significant volumes of drop-in biofuels as the feedstock density supports large-scale operation. However, the development of thermochemical technologies based on low density woody biomass has proven challenging. Amongst other factors, economies of scale are difficult to achieve with low density lignocellulosic feedstock. Other factors include high investment costs to build greenfield biorefineries for production of finished fuels. The technology development of the initial stage of drop-in biofuel production (producing the intermediate) is often at a more advanced level than the second stage, upgrading the intermediate into finished fuels. It is this second stage that most closely resemble petroleum refining and which offers enormous potential for cost saving through refinery integration. While refinery integration and/or co-processing of biobased intermediates in existing refineries are prominently featured in this update, it should not be seen as the

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[119] Low specification fuels such as heating oil or heavy fuel oil (for shipping) may require less upgrading

only solution to upgrading. Freestanding upgrading in biorefineries was extensively covered in the 2014 edition of this report.

The key role of refinery integration and co-processing

As was discussed briefly in the 2014 report, there is considerable potential for good integration between petroleum refineries and biorefineries based on a co-processing strategy. In this update, co-processing is seen as a key strategy for the expansion of drop-in biofuel production, specifically addressing the second stage (upgrading) which seems to be a limiting step in the commercialisation of drop-in biofuels. Success in this process step will enable the accelerated production of liquid bio-based intermediates that can then be upgraded in bulk at existing refineries. Utilisation of existing refinery infrastructure for co-processing of biobased intermediates can unlock the future development and expansion of low carbon drop-in biofuels by creating a commodity market for intermediates, provided the technical and policy considerations can be adequately addressed.

Bio-based intermediates are quite distinct from crude oils as they generally have a higher oxygen content and more reactive chemistry, which will likely impact refinery operations. However, different refinery processing units could serve as potential and suitable insertion points. As discussed in the main report, final selection of insertion points will depend on the refinery configuration and the desired products, as well as the characteristics of the bio-based intermediate and economic considerations (value propositions).

To date, most co-processing research has focused on hydrotreaters or fluid catalytic crackers (FCCs) as potential insertion points. The FCC is the most flexible processing unit as it is able to tolerate a variety of feedstocks and no additional hydrogen inputs are required. FCC catalyst is regenerated on site, which means that catalyst deactivation is easily addressed. The FCC cracks large molecules into smaller ones and is used primarily for gasoline production. So where gasoline is not a primary product, many refineries may not have an FCC and the specific refinery configuration should be matched with the specific requirements for intermediate processing. Cracking of large molecular weight molecules in intermediates such as pyrolysis oils will be a primary objective in the production of drop-in biofuels and the FCC offers an "easier-and less-risky" insertion point in existing petroleum refineries.

Alternatively, hydrotreaters, generally use expensive catalysts that are sensitive to inhibition and deactivation. They are typically not used to crack large molecules into smaller molecules but rather as

processing units for producing finished fuels (fuel blendstocks) by removing contaminants such as sulfur, nitrogen and oxygen (at relatively low concentrations in fossil feeds).

The recent approval of lipid co-processing under ASTM 1655 at 5% blends in existing refineries will allow these co-processed jet fuels to be used in commercial aviation. By creating this immediate market access for co-processed lipids, it is likely that the initial co-processing supply chain will be based on the "conventional/oleochemical" route where hydrotreaters or FCCs are used to co-process/upgrade lipid feedstocks. Lipids have a relatively lower oxygen content (11%), when compared to biomass, and are chemically quite homogeneous, making upgrading to drop-in biofuels significantly easier. In contrast, the biocrudes produced by pyrolysis and HTL routes generate more variable and complex bio-intermediate feedstocks that are more difficult to upgrade into finished fuels. The pyrolysis or HTL pathway is not currently certified under ASTM for producing biojet fuel, either as freestanding upgrading or as a co-processing strategy (and no application is currently under review). It is therefore likely to take longer to develop the supply chains for these intermediates within a co-processing strategy and this is seen as a more long-term strategy. Most likely, biocrudes will initially be inserted in the FCC as the initial strategy based on the lower risk associated with this process, while hydroprocessing might take longer to become established.

Both conventional and advanced routes to drop-in biofuel production have been demonstrated, with the former already at a commercial scale. However, ongoing research is still required to elucidate the behaviour of different biobased feedstocks in different reactors (chemistry and reactions) and the impacts on the product characteristics. Equally important is the need to better determine the fate of the renewable carbon which will be distributed into the various product fractions, i.e., kerosene, gasoline, diesel, etc., produced during normal refinery operation. Renewable carbon content will be a key metric for measuring the carbon reduction potential of finished fuels and form a central part of policies designed to promote this approach. Techno-economic assessments of the different feedstock/reactor co-processing combinations will also be required to determine the economic viability of refinery integration.

Biobased intermediates, e.g. lipids, bio-oils and biocrudes, will originate or be produced from different feedstocks and through different technologies which will result in variation in the chemical characteristics of these intermediates. It is likely that some form of "pretreatment/preliminary upgrading" of biobased intermediates, both lipids and biocrudes, will be needed prior to insertion into a refinery unit for co-processing to reduce the risk for the refinery by stabilisation, removing contaminants, etc. Where this step

is situated at the refinery, a wider range of biobased intermediates could be accepted by the refinery and allow faster commercialisation of co-processing. In parallel, supportive policies and other incentives will be required to encourage refineries to study and advance such co-processing technologies.

Progress in drop-in biofuel commercialisation - oleochemical pathway
With respect to the different technologies, the largest amount of current commercially produced drop-in biofuels are still renewable diesel produced from the hydrotreating of oleochemical feedstocks. It is highly likely that this will remain the most significant source of drop-in fuels in the near term. These conventional drop-in biofuels will be a stepping stone for advanced drop-in biofuels, developing downstream supply chains that will pave the way for other drop-in biofuels to enter the market. The oleochemical technology is also the major supplier of biojet fuels, with dedicated biojet fuel production taking place at World Energy (formerly AltAir) in California, albeit in small volumes, with renewable diesel the major product of this facility. Current world volume of renewable diesel is about 5 billion litres and production continues to be dominated by freestanding facilities based on hydrotreating. There has been a trend toward conversion of existing, disused refinery infrastructure into renewable diesel refineries, including ENI (Italy), Total La Mede (France), and the announcement from Andeavour for a refinery conversion in North Dakota[120].

The two main challenges of the oleochemical pathway were highlighted in the 2014 report as feedstock cost and feedstock sustainability. These challenges are ongoing with oleochemical feedstocks such as vegetable oils often costing more per tonne than finished fuels. The competition between food and fuel has also been an ongoing concern, driving policy in jurisdictions like the EU. However, policies to support climate mitigation in other jurisdictions have played a big role in driving the ongoing production of oleochemical drop-in biofuels, to some extent overcoming the price differential. For example, California and British Columbia have been major destinations for renewable diesel based on the low carbon fuel standards that these regions have in place. The producer incentive for biobased diesels in the USA have also boosted the production of diesels, rather than jet fuels.
With regards to feedstock cost and sustainability, two approaches have been followed to overcome challenges. Companies in this space have aggressively pursued more waste feedstocks, including used

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[120] http://www.andeavor.com/refining/dickinson/dickinson-refinery-renewable-diesel-upgrade-project/

cooking oil, tallow and even brown grease. However, these feedstocks are in limited supply, resulting in increased trade in used cooking oil, tallow and fish fats and oils, For example, countries such as China, New Zealand and Australia are currently exporting these oleochemical feedstocks to Neste facilities in Rotterdam and Singapore. Primarily because further expansion of drop-in biofuels based on these feedstocks will be limited because of availability this has encouraged the development of alternative vegetable oil feedstocks such as jatropha, camelina, carinata, with claims that they do not compete with food and that the crops can be grown on marginal lands. However, the development of entirely new feedstock supply chains (from farmer to processing) have proven challenging and only limited volumes of alternative feedstocks are available.

Progress in drop-in biofuel commercialisation - thermochemical pathways

It is likely that thermochemical technologies based on more widely available feedstocks such as lignocellulose will provide the long-term supply of drop-in biofuels in the future. However, commercialisation of these technologies has been slow.

Although gasification combined with Fischer-Tropsch synthesis has produced commercial, finished fuels for many decades this pathway has used coal or natural gas as the feedstock. This technology pathway was the first to receive ASTM D7566 certification as an alternative jet fuel in 2008, but based on drop-in fuels produced from these fossil feedstocks. Ongoing attempts to commercialise this technology based on biomass has proven problematic. Challenges include, high initial investment costs, syngas cleanup after biomass gasification is possible but expensive, the large scale achieved based on coal and natural gas is problematic with a biomass feedstock and, consequently, biomass is not such a low cost feedstock when new supply chains have to be established.

Although gasification platforms such as plasma gasifiers produce very clean syngas, overcoming the significant challenges of syngas cleanup, plasma gasifiers are expensive to build and operate, and proposed projects such as Solena's facility in the United Kingdom are stalled. Fulcrum Bioenergy, who initially chose plasma gasification as a platform, switched to a bubbling fluidized bed technology, even though these gasifiers generally produce high tar levels. By combining it with steam reforming technology, clean syngas can be produced. The Fulcrum Bioenergy facility is under construction in Nevada and

completion is expected by 2020[121]. Although the company is targeting aviation or biojet fuels, this will only be a portion of the hydrocarbon mixture of FT liquids. Fractionation and possible finishing upgrading steps will still have to be carried out on the FT liquid product blendstock. This again points to the role of refinery integration where existing petroleum refining infrastructure can be used to perform some of these final upgrading steps into finished fuels. One of the key suppliers of small-scale Fischer-Tropsch technology, Velocys, established the ENVIA Energy plant based on gas-to-liquids conversion[122]. Plans for Red Rock Biofuels, based on gasification of wood combined with FT synthesis (provided by Velocys) is still planned and construction commenced in July 2018[123].

While fast pyrolysis is at small commercial scale, the upgrading step of converting the bio-oils into finished fuels has not yet been commercialised. Strategies to overcome the upgrading challenge have been the subject of intense research and development to find new catalysts and to improve the lifespan of catalysts. Alternatively, catalytic pyrolysis technologies have been pursued that produce a liquid intermediate with lower oxygen content and greater stability that is easier to upgrade into finished fuels. However, catalytic pyrolysis suffers from low yields and rapid catalyst deactivation. As mentioned earlier, hydrothermal liquefaction (HTL) can produce a liquid intermediate with a lower oxygen content and the added advantage that it is able to use wet feedstocks. Although this technology has great potential there are significant engineering challenges involved in scaling up a high pressure facility that has not yet progressed past pilot/small demo scale. It should be noted that, even with HTL biocrudes, further upgrading will still be required to produce finished, drop-in biofuels.

Although a more stable bio-oil or biocrude with lower oxygen is highly desirable and easier to upgrade, similar infrastructure will likely still be required for cracking and hydroprocessing to upgrade any liquid intermediate into finished fuels with strict specifications[124]. The techno-economic trade-offs of producing either a low-oxygen intermediate requiring less upgrading, as opposed to a high-oxygen intermediate requiring more upgrading is not clear. Upgrading liquid intermediates from any of the thermochemical liquefaction technologies through refinery integration using a co-processing strategy should be attractive

[121] https://www.prnewswire.com/news-releases/fulcrum-bioenergy-breaks-ground-on-sierra-biofuels-plant-300649908.html
[122] https://www.velocys.com/envia-oct-2017/
[123] https://www.biofuelsdigest.com/bdigest/2018/07/29/red-rock-biofuels-facility-breaks-ground-in-lakeview/
[124] Low specification fuels such as heating oil or heavy fuel oil (for shipping) may require less upgrading

for all cases. However, as detailed in the main body of the report, significantly more research is required to better understand the behaviour of biobased intermediates during co-processing and as well as the resulting economics of the different strategies.

Progress in drop-in biofuel commercialisation - biochemical and hybrid pathways

As stated in the main body of the report, biochemical pathways to drop-in biofuels produce highly functionalised molecules that make them more suitable for applications in the biochemical industry. However, companies such as Amyris, Gevo and Lanzatech have continued to pursue drop-in biofuel production successfully, although still at limited scale. These companies have placed a focus on production of biojet fuels and received ASTM certification for their biojet fuel production pathways. This has given them ready market access and, while biojet fuels continue to be very much in demand, the cost of production has not been much of a consideration. To date a number of flights have used biojet fuel based on the direct sugar to hydrocarbon pathway (DSHC) and the alcohol-to-jet (ATJ) pathways (isobutanol to jet and ethanol to jet).

The past few years have seen an increased interest in Power-to-Liquid fuels, particularly in Europe, as one way of enhancing decarbonisation of transport. This technology is based on carbon capture combined with renewable hydrogen generation through electrolysis of water and synthesis of longer chain hydrocarbons through technologies such as Fischer-Tropsch. This pathway to drop-in fuels offers significant advantages as a drop-in fuel that can be used within existing infrastructure while avoiding sustainability challenges of biomass use. It also serves as a form of energy storage through using excess renewable electricity to create liquid hydrocarbon fuels. However, the biggest challenge for the continued development of Power-to-Liquid fuels will be the ongoing poor economic outlook.

The role of policy in development of drop-in biofuels

Policies offering long-term stability to companies will be key to drop-in biofuels are to be commercialised. However, volumetric mandates for biofuels alone will not be adequate if climate change mitigation is the primary goal. As an example, low carbon fuel standards in jurisdictions like California and British Columbia have played a driving role in promotion of drop-in biofuel production and these types of policies, which reward those biofuels that provide the greatest emission reductions, must become more widespread if drop-in biofuels production and use are to expand. In addition, sectors such as aviation, which is uniquely

reliant on the development of drop-in biofuels, may require specific policies to support the commercialisation and consumption of these biofuels.

The upgrading of most of the "conventional" (oleochemical based) and "advanced" (thermochemical based) drop-in biofuel technologies will result in the production of multiple fuel products, such as diesel, jet fuel and gasoline. As a result, any refinery following a co-processing strategy can help decarbonise many parts of the current transportation sector including aviation, marine, cars and trucks. As drop-in biofuels are fully compatible with existing infrastructure, they can be used in high blends or even neat (depending on fuel standards) to achieve significant emission reductions, in combination with conventional biofuels or on their own. Transportation currently accounts for 14% of the world's carbon emissions and this is expected to grow as the economies of countries such as China, India and Brazil continue to expand. Some transportation sectors such as aviation and marine, cannot easily move to alternatives such as electricity/batteries and will be reliant on lower carbon intensity fuels such as drop-in biofuels. It is anticipated that the production and use of drop-in biofuels will be established using the oleochemical/conventional route in the short-to-mid term, with the thermochemical/advanced route providing the lower cost, lower carbon intensity drop-in biofuels in the mid-to-longer term. As a result, there will be increasing competition for lipid/oleochemical feedstocks in the short term and ongoing competition for low cost, "green" hydrogen. All routes to drop-in biofuel production will require policy support if the world is going to develop lower carbon intensity transportation fuels.

Acknowledgments

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