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Challenges and Opportunities in Fast Pyrolysis of Biomass: Part II

Upgrading options and promising applications in energy, biofuels and chemicals

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Fast pyrolysis for liquids has been developed in recent decades as a fast and flexible method to provide high yields of liquid products. An overview of this promising field is given, with a comprehensive introduction as well as a practical guide to those thinking of applying bio-oils or fast pyrolysis liquids in various applications. It updates the literature with recent developments that have occurred since the reviews cited herein. Part I gave an introduction to the background, science, feedstocks, technology and products available for fast pyrolysis (1). Part II details some of the promising applications as well as pre-treatment and bio-oil upgrading options. The applications include use of bio-oil as an energy carrier, precursor to second generation biofuels, as a biorefinery concept and upgrading to fuels and chemicals.

1. Applications of Bio-Oil

Bio-oil can substitute for fuel oil or diesel in many applications including boilers, furnaces, engines and turbines for electricity generation which was thoroughly reviewed in 2004 (2). Although many aspects have not changed very much, the most significant changes since then include:

- An appreciation of the potential for fast pyrolysis as a pretreatment method, i.e. for bio-oil to be an effective energy carrier
- Greater interest in bio-oil as a precursor for second generation biofuels for transport
- Greater awareness of the potential for fast pyrolysis and bio-oil to offer more versatile process routes to a wider range of products and contribute to biorefinery concept development
- Considerably greater interest in upgrading bio-oil sufficiently for it to be used for heat, power and other applications with greater confidence by users.

Figure 1 summarises the possibilities for applications for bio-oil and the main developments are expanded below.

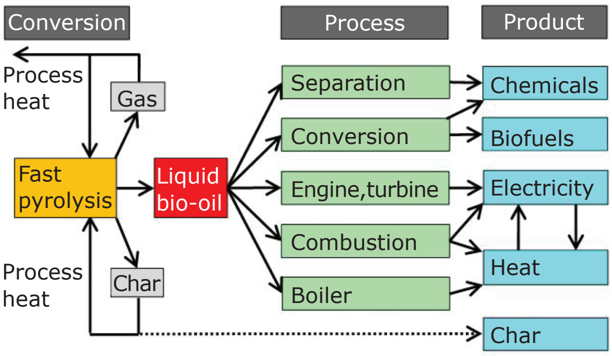

Fig. 1. Applications for fast pyrolysis products

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1.1 Pretreatment Method for Energy Carrier

Biomass is a widely dispersed resource that has to be harvested, collected and transported to the conversion facility. The low bulk density of biomass, which can be as low as 50 kg m^{-3}, means that transport costs are high and the number of vehicle movements for transportation to a large scale processing facility are also very high, with consequent substantial environmental impacts. Conversion of biomass to a liquid by fast pyrolysis at or near the biomass source will reduce transport costs and reduce environmental concerns as the liquid has a density of 1200 kg m^{-3} – more than ten times higher than low density crops and residues. This not only reduces the number of vehicle movements and costs by up to 87%, it also reduces costs of handling and transportation by virtue of it being a liquid that can be pumped. This leads to the concept of small decentralised fast pyrolysis plants of 50,000 to 250,000 tonnes per year for production of liquids to be transported to a central processing plant. It is also possible to consider mixing the byproduct char with the bio-oil to make a slurry to improve the energy content of the product, but the pyrolysis process will then require that its process energy needs are met from another source.

Adoption of decentralised fast pyrolysis with transportation of the resultant liquid to a central gasification and fuel synthesis plant has both technical and economic advantages and disadvantages as summarised in **Table I**. The impact of inclusion of fast pyrolysis as a pretreatment step on biomass-to-liquids (BTL) cost and performance has been analysed (3).

1.2 Co-Firing

Co-processing of biomass with conventional fuels is potentially a very attractive option that enables full economies of scale to be realised as well as reducing the problems of product quality and clean up. Most current co-firing applications are those where the biomass fuels are added to the coal feed and this is widely practised at up to 5% on the energy demand of the power station. A few applications involve conversion to a fuel gas *via* gasification followed by close coupled firing to the power station boiler. There are also some successful examples of co-firing fast pyrolysis liquids in coal fired and natural gas fired power stations (4, 5).

1.3 Fast Pyrolysis Based Biorefinery

While biorefineries are not new, the recognition of their strategic and economic potential is recent. A biorefinery can be defined as the optimised performance of the use of biomass for materials, chemicals, fuels and energy applications, where performance relates to costs, economics, markets, yield, environment, impact, carbon balance and social aspects. In other words, there needs to be optimised use of resources, maximised profitability, maximised benefits and minimised wastes.

The large majority of chemicals are manufactured from petroleum feedstocks. Only a small proportion of the total oil production, around 5%, is used in chemical manufacture but the value of these chemicals is high and contributes a comparable revenue to fuel and energy products. There is a clear economic advantage in building a similar flexibility into the biofuels market by devoting part of the biomass production to the manufacture of

Table I Comparison of Bio-Oil Gasification to Solid Biomass Gasification to Generate Syngas (3)

Bio-oil *vs.* solid biomass	Impact on capital cost and product cost	Impact on overall process performance
Transport costs for bio-oil	Lower	Higher
Handling and storage costs for bio-oil	Lower	None
Very low alkali metals in bio-oil	Lower	Higher
Liquid bio-oil feeding to a gasifier, particularly pressurised	Lower	Higher
Changed gas cleaning requirements when using bio-oil	Lower	Higher
Need for additional fast pyrolysis process	Higher	Lower

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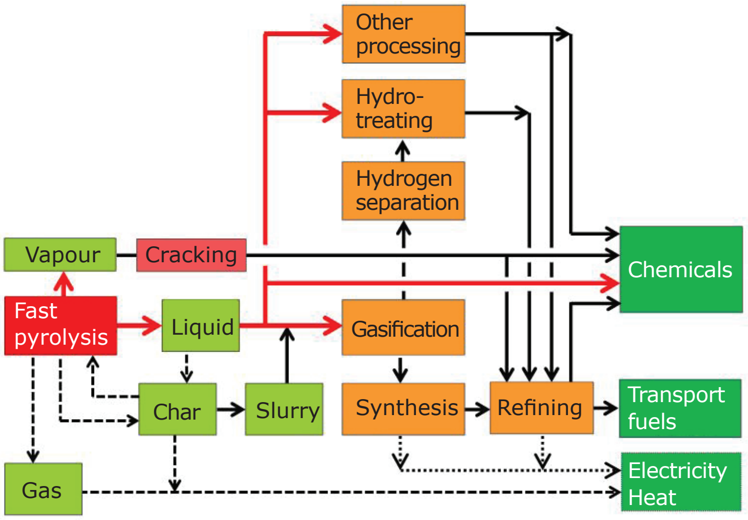

Fig. 2. Fast pyrolysis based biorefinery

chemicals. In fact, this concept makes even more sense in the context of biomass because it is chemically more heterogeneous than crude oil and conversion to fuels, particularly hydrocarbons, is not so cost effective. **Figure 2** shows fast pyrolysis at the heart of a biorefinery.

A key feature of the biorefinery concept is the co-production of fuels, chemicals and energy. As explained earlier, there is also the possibility of gasifying biomass to make syngas, a mixture of hydrogen and carbon monoxide for subsequent synthesis of hydrocarbons, alcohols and other chemicals. However, this route is energy intensive so much of the energy content of the biomass is lost in the processing. Therefore, electricity generation may be the most efficient use of biomass (6).

Since the empirical chemical composition of biomass, approximately $(CH_2O)_n$, is quite different from that of oil $(CH_2)_n$, the range of primary chemicals that can be easily derived from biomass and oil are quite different. Hence, any biomass chemical industry will have to be based on a different selection of simple 'platform' chemicals than those currently used in the petrochemical industry. Since the available biomass will inevitably show major regional differences, it is quite possible that the choice of platform chemicals derived from biomass will show much more geographical variation than in petrochemical production.

2. Bio-Oil Upgrading

Bio-oil can be upgraded in a number of ways: physically, chemically and catalytically. While this has been extensively reviewed (2, 7–10), some interesting and potentially important developments have taken place in recent years concerning approaches to upgrading, especially for biofuels. There are a number of objectives for upgrading of which the main ones are:

(a) Improvement of bio-oil quality to overcome or reduce one or more of the quality deficiencies (summarised in Part I, **Table III** (1))
(b) Production of chemicals
(c) Removal of oxygen to provide hydrocarbon biofuels.

2.1 Bio-Oil Quality Improvement

The most important properties that inhibit widespread use of bio-oil are:

- Phase separation from use of wet feedstock and/or secondary cracking of vapours leading to high water content in the liquid product. Phase separation cannot be reversed except through relatively high additions of co-solvents such as ethanol
- Incompatibility and immiscibility with conventional fuels from the high oxygen content of the bio-oil
- High solids content that affect catalysts and utilisation in engines and burners
- High viscosity that hinders pumping and combustion and which cannot readily be controlled by raising temperature as for heavy fossil fuels due to temperature sensitivity
- High water content that lowers heating value but also lowers viscosity
- Chemical or thermal instability which limits the use of higher temperatures for controlling properties
- High acidity leading to corrosion in storage and utilisation.

2.1.1 Filtration

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, much lower than reported for biomass oils produced in systems using only cyclones. This gives a higher quality product with lower char (11), however accumulated char on the filter medium is catalytically active and potentially cracks the vapours, reduces yield by up to 20%, reduces viscosity and lowers the average molecular weight of the liquid product. There is limited information available on the performance or operation of hot vapour filters, but they can be specified and perform similarly to hot gas filters in gasification processes.

Diesel engine tests performed on crude and on hot-filtered oil showed a substantial increase in burning rate and a lower ignition delay for the latter, due to the lower average molecular weight for the filtered oil (12). Hot gas filtration has not yet been demonstrated over a long-term process operation. A little work has been done in this area by the US Department of Energy National Renewable Energy Laboratory (NREL), USA and VTT Energy, Finland (11), and by Aston University (13), but very little has been published.

Liquid filtration to very low particle sizes of below around 5 μm is very difficult due to the physico-chemical nature of the liquid and usually requires very high pressure drops and self-cleaning filters, although improvement is claimed with filter pores of around 10 μm.

2.1.2 Solvent Addition

Polar solvents have been used for many years to homogenise and reduce the viscosity of biomass oils. The addition of solvents, especially methanol, showed a significant effect on the oil stability. Diebold and Czernik (14) found that the rate of viscosity increase (‘ageing’) for the oil with 10 wt% of methanol was almost twenty times less than for the oil without additives. Use of co-solvents to compatibilise bio-oil with other sustainable liquid fuels as blends is covered below.

2.1.3 Emulsions

Pyrolysis oils are not miscible with hydrocarbon fuels but they can be emulsified with diesel oil with the aid of surfactants. A process for producing stable micro-emulsions with 5–30% of bio-oil in diesel has been developed at CANMET, Canada (15). The University of Florence, Italy, has worked on emulsions of 5 to 95% bio-oil in diesel (16–18) to make either a transport fuel or a fuel for power generation in engines that does not require engine modification to dual fuel operation. There is limited experience of using such fuels in engines or burners, but substantially higher levels of corrosion/erosion were observed in engine applications compared to bio-oil or diesel alone, sometimes to the extent of limiting operation to less than 1 hour. A further drawback of this approach is the cost of surfactants that provide longer term stability and the high energy required for emulsification.

2.1.4 Blends

More recently, some success has been achieved through production of blends of bio-oil with a variety of co-solvents and other sustainable or green fuels as well as conventional transport fuels. Bio-oil by itself is considered too demanding for simple direct use due to acidity, ageing, particulates and incompatibility with fossil fuels. Therefore some exploratory work was initiated in 2012 to produce homogenous blends of bio-oil with bio-diesel and an alcohol co-solvent – both ethanol and butanol (19). A key result was that single phase and stable blends of bio-oil, biodiesel and either ethanol or butanol could be prepared which utilised the whole bio-oil including the water content. Areas of miscibility and non-miscibility were identified and the work was published (19). The shorter term objective is to address ferry needs rather than intercontinental shipping and also to satisfy the new requirements for low sulfur fuels.

A key requirement is to maximise the use of bio-oil, maximise the sustainability of the resultant blend by use of renewable solvents, and satisfy marine oil specifications, of which flash point above 60°C is key. Subsequently, the early work was extended to consider diesel and marine gasoil as hydrocarbons in a four-component blend. The second phase of this work is nearing completion after testing a wide range of co-solvents.

2.2 Chemicals

Although bio-oil contains in excess of 1000 individual chemicals, few are present in sufficient concentrations to justify recovery. This has been reviewed by Radlein (20). The largest single component in bio-oil is in fact water. Other chemicals of value include food flavouring often known as ‘liquid smoke’ (21) and until recently

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the only commercial application of fast pyrolysis was production of liquid smoke by Red Arrow of Wisconsin, USA. Hydroxacetaldehyde or glycolaldehyde can be isolated from bio-oil (22) and is considered as the most reactive browning compound participating in the Maillard reactions (23). Levoglucosan, an anhydrosugar, can be readily recovered in high purity and high yield but until recently was perceived as having limited market value. This has been reviewed (24). More attention is currently being paid to the potential for hydrolysis to sugars (25). High purity acetic acid is recovered from slow pyrolysis liquids by Profagus in Germany (26), together with other chemicals when market conditions are right.

2.3 Hydrocarbon Biofuels

Direct production of high yields of liquids by fast pyrolysis inevitably caused attention to focus on their use as biofuels (sustainable transport fuels) to supplement and replace fossil fuel derived transport fuels. However, the high oxygen content of bio-oil and non-miscibility or incompatibility with hydrocarbon fuels has prevented simple adoption of bio-oil as a transport fuel.

The main methods for upgrading bio-oil to transport fuels are summarised in **Figure 3**:

- Hydrodeoxygenation of bio-oil to a substantially de-oxygenated product
- Catalytic vapour cracking of fast pyrolysis vapours (i.e. close coupled) to aromatics that can be followed by hydrodeoxygenation and/or introduction into a refinery
- Partial upgrading by hydrodeoxygenation followed by introduction into a refinery
- Direct introduction of crude bio-oil into a refinery
- Gasification to syngas followed by synthesis to hydrocarbons or alcohols.

2.3.1 Hydrodeoxygenation

Hydro-processing of liquid bio-oil rejects oxygen as water by catalytic reaction with hydrogen. This is a separate and distinct process to fast pyrolysis that can therefore be carried out remotely. The process is typically high pressure (up to 20 MPa) and moderate temperature (up to 400°C) and requires a hydrogen supply or source (27). Most attention is now focused on multiple step processes with increasingly severe conditions starting with a stabilisation step to improve temperature stability followed by more orthodox hydrotreating. More or less full hydrotreating gives a naphtha-like product that requires orthodox refining to derive conventional transport fuels. This would be expected to take place in a conventional refinery to take advantage of know-how, existing processes and economies of scale. A projected typical yield of naphtha equivalent from biomass is about 20% by weight or 55% in energy terms excluding provision of hydrogen (9). Inclusion of hydrogen production adds a significant inefficiency due to use of biomass to generate hydrogen for example by gasification and shifting the CO. This reduces the yields to around 15 wt% or 40% in energy terms. The process can be depicted by the following conceptual reaction (Equation (i)):

$$CH_{1.32}O_{0.43} + 0.77\ H_2 \rightarrow CH_2 + 0.43\ H_2O \qquad (i)$$

The catalysts originally tested in the 1980s and 1990s were based on sulfided cobalt molybdenum or nickel molybdenum supported on alumina or aluminosilicate and the process conditions are similar to those used in the desulfurisation

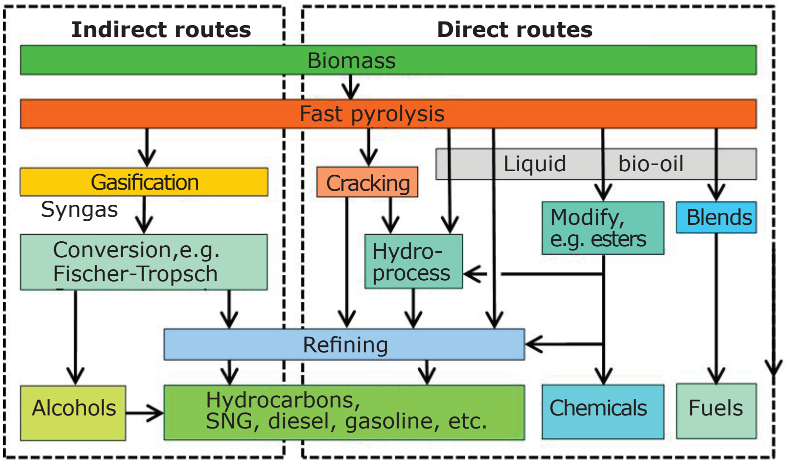

Fig. 3. Overview of fast pyrolysis upgrading methods

of petroleum fractions. However a number of fundamental problems arose including that the catalyst supports of typically alumina or aluminosilicates were found to be unstable in the high water content environment of bio-oil and the sulfur was stripped from the catalysts requiring constant re-sulfurisation. The main activities were based at Pacific Northwest National Laboratory (PNNL), USA by Elliott (28–30) and at Université catholique de Louvain (UCL) in Louvain la Neuve in Belgium by Maggi *et al*. (31, 32). This area has been thoroughly reviewed (7). A recent design study of this technology for a biomass input of 2000 dry tonnes per day for production of gasoline and diesel has been carried out by PNNL (33). A comprehensive review of unsupported metal sulfide hydrotreating catalysts was published in 2007 (34).

More recently, attention turned to precious metal catalysts on less susceptible supports, and considerable academic and industrial research has been carried out. Of note is the work by UOP in Chicago, USA, (now Honeywell UOP) with PNNL in the USA to address the scientific and technical challenges and develop a cost effective process (35). Model compounds were used initially to understand the basic processes (36) and both whole oil and fractions have been evaluated. Tests have been carried out on both batch and continuous flow processes focussing on an initial low temperature stabilisation step followed by more extensive catalytic de-oxygenation using different metal catalysts and processing conditions to give a range of products including petroleum refinery feedstock. Remaining challenges include complete deoxygenation especially of phenols without saturation with hydrogen.

A key aspect is production of hydrogen. Since the hydrogen requirement is significant, it should be renewable and sustainable. Few refineries have a hydrogen surplus, so this has to be provided. There are many ways of providing hydrogen such as gasification of biomass followed by shifting to H_2 then scrubbing CO_2. Product bio-oil or the aqueous phase from a phase separated product can be steam reformed to hydrogen; or hydrogen can be generated locally by electrolysis of water preferably using renewably produced electricity. Supply of hydrogen from external sources is unlikely to be feasible due to very high cost of storage and transport. The necessary purity of hydrogen is unknown, but some CO shifting may take place in the hydroprocessing reactor removing the need for dedicated shift reactors. The high cost of hydrogen means that unused hydrogen would have to be recovered and recycled as only a fraction of the hydrogen would be utilised due to the need for high hydrogen partial pressures. Recovery and recycling of unused hydrogen is both technically and economically challenging.

There is increasing interest in supercritical processing of bio-oil to either improve the properties of bio-oil or to de-oxygenate it to a hydrocarbon fuel. The supercritical fluids studied include water, CO_2, methanol, ethanol, butanol and cyclohexane using traditional CoMo type catalysts, precious metals such as platinum, palladium and ruthenium on inert supports such as carbon or cracking catalysts including HZSM-5. The results are mixed with no clear conclusions on the efficacy of this route. High pressures are still required as well as recovery of the fluids involved. Many researchers report an improvement in bio-oil properties such as lower acid levels and higher esters, but there has been a disappointing absence of significant moves towards real hydrocarbon bio-fuels. There continues to be an interest in use of model compounds even though it is impossible to adequately represent the complexity of bio-oil with single compounds or even groups of so called representative compounds.

2.3.2 Catalytic Vapour Cracking (Close Coupled)

Cracking, usually over zeolites, rejects oxygen as CO_2, as well as water, summarised in the conceptual overall reaction below (Equation (ii)):

$$C_{0.99}H_{1.32}O_{0.43} + 0.26\ O_2 \rightarrow 0.65\ CH_{1.2} + 0.34\ CO_2 + 0.27\ H_2O \quad \text{(ii)}$$

The process takes place in two stages: firstly cracking which deposits carbon or coke on the catalyst surface, which is then burned off in a second reaction. In this case the oxygen is ultimately mostly rejected as CO_2, with some water, from burning off the carbon on the coked catalyst. This lowers the carbon efficiency of the process compared to hydrodeoxygenation, but avoids the need for hydrogen and pressure.

Cracking takes place at atmospheric pressure either with *in situ* catalyst or in a close coupled process. There is no requirement for hydrogen or pressure. The projected yield is around 18 wt% aromatics and the process is understood to be the basis for the recently abandoned Kior process (37, 38). This process is believed to have been based on a first stage of zeolite cracking, possibly modified with metals, followed by hydrotreating to deliver hydrocarbon transport fuels. Although a

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large demonstration plant was built in Mississippi, deliveries of products were consistently below claims and expectations, and the projected yields were not met and appeared optimistically high. A similar process is under development by Anellotech (39).

Early work by NREL added a close coupled secondary reactor to the fast pyrolysis process in which vapours passed through a close coupled fixed bed of ZSM catalyst (40). This has the advantage of providing independent control of the temperature and residence of pyrolysis vapours over the catalyst.

Among cracking catalysts, ZSM-5 has attracted most attention due to its shape selectivity to aromatics, with promoters such as gallium or nickel (41). A key disadvantage is that the catalyst rapidly cokes which requires frequent regeneration as in a fluid catalytic cracking (FCC) unit in a conventional refinery. Oxygen is thus substantially removed as CO and CO_2 (as well as H_2O) compared to solely H_2O in hydrodeoxygenation. Production of aromatics is also likely to be of significant interest to the chemicals sector, where aromatics are the second largest global petrochemicals sector.

A complementary approach is to incorporate cracking catalysts in the pyrolysis reactor which offers a more compact reaction system, but compromises have to be made between optimum pyrolysis conditions and optimum catalysis conditions. This area has attracted much increased interest in recent years. Although some advantages result in improvements to yield and quality of liquids, the catalyst has to operate at the same temperature as pyrolysis (or *vice versa*) and the necessary contact times for fast pyrolysis are not optimal for catalytic cracking. However this could operate as the first step in a multi-stage process followed by secondary vapour processing utilising process conditions more suitable for vapour phase cracking. This approach offers technical and economic advantages especially when combined with catalyst development and is the approach adopted by Inaeris Technologies, USA (42); this also allows for recycling and processing of used catalyst.

2.3.3 Partial Upgrading by Hydrodeoxygenation Followed by Introduction into a Refinery

Direct incorporation of bio-oil into a refinery was long thought to be unacceptable due to the poor miscibility of bio-oil with conventional refinery streams and the potential for catastrophic blockage of a non-mixed bio-oil component in upgrading processes such as hydrocracking. Therefore partial hydrodeoxygenation to an upgraded and hydrocarbon miscible product was seen as one of the more attractive solutions. However, due to immiscibility, simple addition of bio-oil to any refinery stream would lead to two phase flow into whatever upgrading process was selected. Since all upgrading processes operate at moderate to high temperatures, this will result in phase separation of the bio-oil above around 100°C and subsequent polymerisation at higher temperatures leading to blockage of the preheaters or the upgrading unit which would be very costly to remedy. Since bio-oil hydrodeoxygenation is conventionally carried out in stages, partial hydrodeoxygenation will require less hydrogen and result in a lower cost process. One problem is defining how much oxygen has to be removed for miscibility and secondly how the miscibility of an upgraded bio-oil which can be black, can be measured when mixed with a conventional black refinery stream. This approach has not progressed very far for both these reasons as well as substantial doubts about the extent of development required in the refinery. However, here is still good reason to believe that this approach offers significant potential.

2.3.4 Direct Addition of Bio-Oil to a Fluid Catalytic Cracking Unit

The realisation that conventional refineries provide an enormous asset in fuel processing and production with their technical know-how and economies of scale, has led to wider consideration of partial upgrading to a refinery compatible material intermediate for subsequent refinery processing.

A report by Hydrocarbon Processing for the future of FCC and hydroprocessing in modern refineries states that: “Biomass-derived oils are generally best upgraded by HZSM-5 or ZSM-5, as these zeolitic catalysts promote high yields of liquid products and propylene. Unfortunately, these feeds tend to coke easily, and high TANs and undesirable byproducts such as water and CO_2 are additional challenges” (43). It was recognised that some upgrading may be necessary prior to introduction of bio-oil (44). Integration into refineries by upgrading through cracking or hydrotreating has been reviewed by Huber and Corma (45).

Most attention focused on hydrotreating bio-oil as a means of reducing the oxygen content to a level that is compatible with refinery operation or is substantially or totally miscible with refinery streams or has sufficiently low oxygen content to be stable and temperature insensitive. Another approach has been deoxygenation of bio-oil over zeolites followed by hydrodeoxygenation as practiced by KiOR Inc, USA, but this activity has now been wound up.

One approach is to introduce raw bio-oil into the riser of a FCC unit. As bio-oil cannot be preheated without decomposing and blocking the feeder, it has to be fed cold which imposes an additional thermal load. In addition, when the bio-oil contacts hot regenerated catalyst it will evaporate and crack into vapours and char or coke. There is therefore a significant loss of efficiency in carbon utilisation of potentially 35% from Equation (ii) and an increased coke burden in the FCC regenerator. Hydrodeoxygenation tends to retain the majority of the carbon while losing the oxygen as water, but there is a significant inefficiency if the hydrogen is generated from biomass, such as by gasification and shifting. However the concept appears promising as the requirement for independent upgrading is obviated. Some preliminary results have been published (46, 47). Historically, one approach to upgrading bio-oil over zeolites was re-evaporation of bio-oil and passing the vapours through zeolites. This work was pioneered by Bakhshi *et al*. and this provides some insight into the potential of this approach as well as the effect of different catalysts (48, 49).

The ultimate ambition of most work in this area is a 'one-pot' approach where full deoxygenation to an acceptable product would be accomplished. To date this has not been as successful with low yields and extensive byproducts requiring utilisation or disposal. There appears to be a realisation that fast pyrolysis is a crude primary conversion step giving an unusually complex product that is likely to be best processed in an optimised sequence of carefully considered conversion steps.

2.3.5 Gasification of Bio-Oil for Synfuels

A recent concept that has attracted much interest is the decentralised production of bio-oil or bio-oil/char slurries for transportation to a central process plant for gasification and synthesis of hydrocarbon transport fuels, for example by Fischer Tropsch synthesis or alcohols. This is depicted above in **Figure 2**. Although there is a small energy penalty from the lower pyrolysis energy efficiency, transportation energy and additional bio-oil gasification stage, this is more than compensated by the economies of scale achievable on a commercial sized gasification and transport fuel synthesis plant (3).

Although the concept of very large gasification plants of 5 GW or more has been promoted (50) based on importation of biomass on a massive scale to an integrated plant, there are significant obstacles to be overcome. Decentralised fast pyrolysis plants of up to 100,000 tonnes per year or 12 tonnes per hour are currently feasible and close to being commercially realised. Bio-oil gasification in an entrained flow oxygen blown pressurised gasifier is also feasible such as a Texaco or Shell system, with the added advantage that feeding a liquid at pressure is easier than solid biomass, offers lower costs and the gas quality under such conditions is likely to be higher than from solid biomass. Future Energy (now Siemens, Germany) has successfully conducted pressurised oxygen blown gasification tests on both bio-oil and bio-oil/char slurries (51, 52) and this approach, known as the bioliq process, is under development at Karlsruhe Institute of Technology (KIT) in Germany where bio-oil/char slurries from a twin screw pyrolysis reactor are gasified and converted to biofuels (53).

There is increased interest in smaller scale economic synfuels technology such as the Velocys®, USA, microchannel reactor (54). This is claimed to overcome the scale problems of conventional Fischer Tropsch technology in that economic operation is feasible at small scale making it more suitable to biomass based processes.

2.3.6 Other Methods and Routes

A wide variety of methods and catalysts have been investigated in recent years with some examples listed below. Many are attempts to conflate different processes, reactions and catalysts to move towards the 'one-pot' approach mentioned earlier, but most have misjudged the chemical complexity of bio-oil. It is important to emphasise the importance of maximising yield and minimising unwanted reactions especially minimising residues since these will have to be disposed of at a potential cost as well as lowering efficiency:

- Acid cracking in supercritical ethanol
- Aqueous-phase reforming + dehydration + hydrogenation

- Dicationic ionic liquid such as $C_6(mim)_2-HSO_4$
- Esterification of pyrolysis vapours
- Esterification of liquid bio-oil
- Hydrogenation-esterification over bifunctional Pt catalysts
- Reactive distillation
- Solid acid catalysts such as $40SiO_2/TiO_2-SO_4^{2-}$
- Solid base catalysts such as $30K_2CO_3/Al_2O_3$-NaOH
- Steam reforming over orthodox and more unusual catalysts
- ZnO, MgO and Zn-Al and Mg-Al mixed oxides.

3. Conclusions

The liquid bio-oil produced by fast pyrolysis has the considerable advantage of being storable and transportable, as well as having the potential to supply a number of valuable chemicals. In these respects it offers a unique advantage. Fast pyrolysis has some basic and essential requirements if good yields of good quality bio-oil are to be derived. The potential of bio-oil is increasingly being recognised, with a rapid growth in research into improving bio-oil properties particularly for dedicated applications and for biofuel production. Much of the research is still at a fundamental scale even to the use of model compounds and mixtures of model compounds that purport to represent whole bio-oil. It is doubtful if a limited component mixture can adequately represent the complexity of bio-oil. Some of the most interesting and potentially valuable research is on more complex and more sophisticated catalytic systems and these will require larger scale development to prove feasibility and viability.

Biorefineries offer considerable scope for optimisation of fast pyrolysis based processes and products, and these will require development of component processes in order to optimise an integrated system. They will necessarily include provision of heat and power for at least energy self sufficiency.

There is an exciting future for both fast pyrolysis and bio-oil upgrading as long as these are focused on delivering useful and valuable products.

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