Report on the Most Suitable Technology for DMB Production from Bio-oil and Syngas

Deliverable Number: 4.5
Contractual Deadline: M42
Date: 23 May 2013
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Dissemination status: PU

With the support of the Seventh Framework Programme.

Contents

1 INTRODUCTION

The focus of this report is to summarise the potential diesel biofuels and necessary reagents such as alcohols that have been considered in the project and evaluate their potential. This considers the feedstocks from the EU and LA, solid residues from acid hydrolysis, the production of alcohols for esterification and the means of obtaining the hydrogen needed for hydrotreating.

2 PRODUCTS

Figure 1 summarises the processes and products that are derivable from biomass and the residues from ethyl levulinate production in order to put this deliverable into context with the overall project. It includes the provision of heat and power to provide an energetically self sufficient process utilising only biomass.

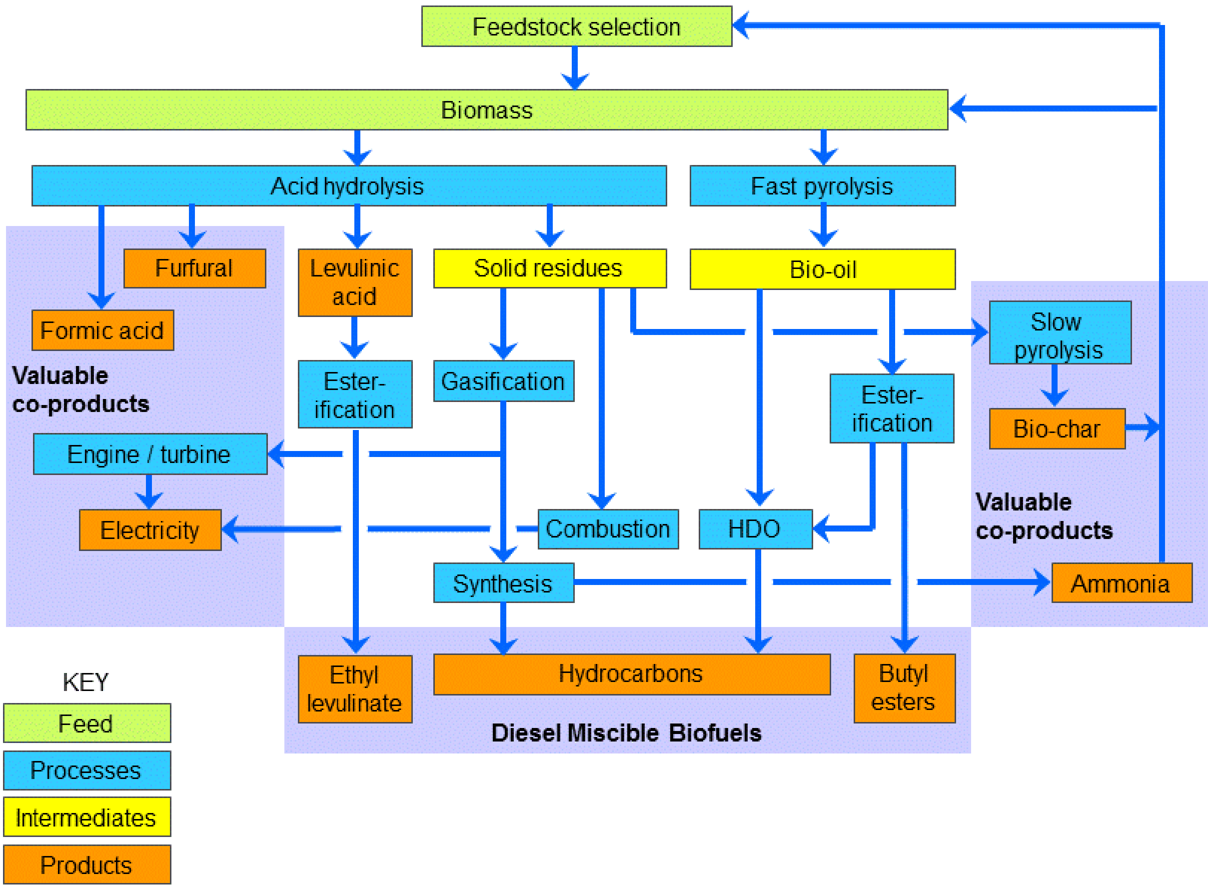

Figure 1 Summary of processes and products that may be derived from the DIBANET biorefinery

Table 1 includes products and necessary reagents such as alcohols and hydrogen from biomass. By-products are also formed such as formic acid and furfural which could improve the viability of an integrated process if economic recovery is possible. In addition an acid hydrolysis residue (AHR) is also produced from levulinic acid production which has been considered for conversion to valuable products.

Table 1 Summary of potential products from the Dibanet projects

Product	Miscibility with diesel	Feed	Process 1	Process 2	Process 3	Valuable byproducts	Residues of minimal value i.e. waste	Uncertainty	Approx yield wt.% from biomass*
1 Synthetic gasoline	Full	Biomass	Fast pyrolysis	Catalytic cracking	Olefin oligerom-erisation	Light hydrocarbons fuel gas		High	20
2 Synthetic diesel, gasoline, kerosene	Full	Biomass	Gasification of solid biomass	Fischer Tropsch & related processes	Fractionation and refining	Light hydrocarbons		Medium	18
3 Synthetic diesel, gasoline and kerosene	Full	Bio-oil	Gasification of liquid bio-oil	Fischer Tropsch	Fractionation and refining	Light hydrocarbons		Low	16
4 Synthetic hydrocarbons	Full	Bio-oil	HDO of bio-oil	Fractionation	Refining			Medium	22
5 Hydrocarbons	Full	AHR #	HDO	Fractionation	Refining	Carbon		Very high	12
6 Hydrocarbons	Full	Esterification residue	HDO	Fractionation	Refining			Very high	20
7 Bio-oil	Full with co-solvent	Biomass	Fast pyrolysis			Char		Very low	70
8 Butyl esters	Partial	Bio-oil	Esterification with butanol	Fractionation		Heavy residue		Medium	14
9 Ethanol	Low	Biomass	Gasification	Synthesis	Distillation	CO_2		Low	45

						Methanol, Propanol, Butanol			
9 Ethanol	Low	Bio-oil	Gasification	Synthesis	Distillation	CO_2 Methanol, Propanol, Butanol		Low	45
10 Ethanol	Low	Syngas	Fermentation	Distillation		CO_2 +others not known		High	60
11 Butanol	Low	Biomass	Hydrolysis	Fermentation	Distillation	CO_2	Acetone, Ethanol	Low	40
12 Butanol	Low	Syngas	Fermentation	Distillation		CO_2 +others not known		High	nk
13 Hydrogen	na	Biomass	Gasification	Shift	CO_2 removal	CO_2		Low	5
14 Hydrogen	na	AHR	Gasification	Shift	CO_2 removal	CO_2		Medium	5
15 Power	na	Biomass	Gasification	Engine or turbine		Heat		Low	30-35% energy
15 Power	na	Biomass	Combustion	Steam turbine		Heat		Very low	25-30% energy
16 Power	na	AHR #	Gasification	Engine or turbine		Heat		Low	17-22% energy
17 Power	na	AHR #	Combustion	Steam turbine		Heat		Very low	12-17% energy

NOTES
AHR = acid hydrolysis residue
# assumes 65% yield of AHR from process 1
* for partial processes, efficiencies are additive

3 EVALUATION METHODS

There are a range of methods for evaluating and comparing products and processes to identify preferred products and routes. These include, but not necessarily in order of importance:

1. Miscibility with diesel
2. Product yield in mass terms or process mass performance – main product
3. Product yield in mass terms or process mass performance – all valuable products
4. Product yield in energy terms or process energy efficiency – main product
5. Product yield in energy terms or process energy efficiency – all valuable products
6. Energy ratio of main product (energy in main product compared to energy inputs)
7. Energy ratio of all valuable products (energy in products compared to energy inputs)
8. Process capital cost for main product
9. Process capital cost for all valuable products
10. Main product production cost
11. Production cost of all valuable products
12. Viability of process for main product as Return on Investment, NPV or DCF rate of return
13. Viability of process for all valuable products as Return on Investment, NPV or DCF rate of return
14. Environmental impacts, for example CO_2 emissions compared to fossil fuel derived products, although there are at least 15 different measures available
15. Socioeconomic factors, especially employment.

In all cases, the disposal of all products not considered valuable is required, such as by incineration or bio-degradation.

4 VALUABLE PRODUCTS FROM BIOMASS AND DIBANET PRODUCTS

4.1 Synthetic hydrocarbons - diesel, gasoline, kerosene

Hydrocarbons can be produced in a number of ways including:

1. Fast pyrolysis to bio-oil followed by hydrodeoxygenation which has not been attempted but is known to be successful.
2. Fast pyrolysis to bio-oil followed by gasification to syngas followed by synthesis such as Fischer Tropsch which has not been attempted but all steps are known to be feasible.
3. Gasification of solid biomass to syngas followed by synthesis such as Fischer Tropsch which has not been attempted but is known to be successful
4. Hydrodeoxygenation of esterification residue which has not been attempted.
5. Hydrodeoxygenation of AHR which has not been attempted.

The product from cases 1, 4 and 5 above can have various degrees of oxygen removal according to the conditions employed. The product could be diesel miscible, or could be fed to a conventional refinery for refining into a conventional diesel. The product from cases 2 and 3 would be a completely compatible hydrocarbon.

All these processes have relatively low efficiency in mass (typically 15 to 20 wt.%) and energy (typically 40 to 50%) terms.

The hydrocarbons would all be miscible with diesel.

4.2 Bio-oil

Fast pyrolysis for liquids is particularly interesting as the liquid is produced in high yields and can be easily stored and transported; and used for energy, chemicals or as an energy carrier. Pyrolysis has been applied for thousands of years for charcoal production but it is only in the last 30 years that fast pyrolysis has become of considerable interest because the process directly gives high yields of liquid of up to 75 wt.%. This can be used directly in a variety of applications or used as an efficient and effective energy carrier. Bio-oil was used for esterification in the next section.

Until acid hydrolysis residues were available from Limerick, fast pyrolysis focussed on biomass as miscanthus and bagasse. Experiments were successful and delivered good quality bio-oil in yields of around 60-65 wt.%. After the first year it became clear that AHR could not be successfully fast pyrolysed, so attention focussed on gasification which was successful.

An alternative use for bio-oil is as a diesel miscible liquid when used with a co-solvent such as butanol (or bio-butanol). Initial work focussed on three component mixtures [1] while more recent, as yet unpublished research, has demonstrated successful four component blends with diesel. Levels of up to 30 wt.% bio-oil are possible.

Bio-oil can also be gasified to syngas for production of hydrocarbons (3 in Table 1) or alcohols as esterification reagents

4.3 Butyl esters

Esterification is well known and is usually carried out using sulphuric acid as a catalyst. Within Dibanet, novel solid acid catalysts were developed for esterification of levulinic acid to ethyl levulinate and these novel catalysts were also applied to bio-oil to replace mineral acids, reduce acid handling and recycle requirements and produced a significantly different set of esters with potential use as diesel miscible biofuels and/or speciality chemicals with premium values.

Esterification with solid acid catalysts was attempted with ethanol, propanol and butanol with the most successful results in terms of yield and selectivity being from butanol. A water white product was derived that had a substantially different composition than esters produced using sulphuric acid as the catalyst. The yield from biomass was around 13-14 wt.%.

There is a substantial heavy organic residue from esterification of around 70 wt.%, which can potentially be hydrotreated to give a substantially de-oxygenated product suitable for feeding to a refinery or used as a DMB. This has not been investigated.

4.4 Alcohols

In a maximum sustainability process, alcohols for esterification would be produced from biomass. Three main processes are available:

1. Thermal gasification of biomass or bio-oil to syngas followed by synthesis of mixed alcohols
2. Thermal gasification of biomass or bio-oil to syngas followed by fermentation of syngas to ethanol as currently under development (e.g. Lanzatech and Ineos), or to butanol which is not known to have been attempted
3. Fermentation of hydrolysed biomass for ethanol or butanol

Routes to ethanol are being widely developed and commercialised while routes to butanol are still under development.

4.5 Hydrogen

Upgrading of bio-oil and residues identified in Table 1 will require considerable quantities of hydrogen. This can be derived from syngas by shifting the carbon monoxide to hydrogen and stripping out the CO_2. This is a well-established process and only suitable for large scale applications. Smaller scale hydrogen requirements, especially are probably best met by local electrolysis of water.

4.6 Power

Any process for production of diesel miscible biofuels will require a range of utilities of which power is a significant requirement. While power would typically be purchased from the grid, one key objective of Dibanet was to design self-sufficient processes with all utilities of power and heat being generated from residues and/or fresh biomass. There are a range of standard processes for combustion of biomass or wastes coupled with a steam turbine for power generation. This is generally very inefficient for generation of power, with small scale processes being the least efficient. An advantage is that combustion is very well developed and widely practiced around the world so has the lowest uncertainty and lowest risk, both technically and economically, of all the conversion process studied.

Gasification based power generation would typically utilise engines at up to around 10 MWe and gas turbines above this level. The uncertainty lies in the gas quality requirements which are more demanding for turbines than engines and the extent of downgrading power output from low quality fuel gas. Engines are more tolerant of likely contaminants but are less suitable for Combined Heat and Power (CHP) systems while gas turbines require much lower contaminant levels but are more suitable for CHP and/or cogeneration, especially at larger plant sizes when efficiencies can exceed 40%.

5 CONCLUSIONS

New routes to diesel miscible biofuels need to be thoroughly investigated and evaluated to provide a sound development of renewable technologies for the next 40 or so years. Most attention has focussed on biological and thermal routes, but recent years have seen substantial growth in more imaginative chemical and hybrid routes for production of biofuels and these should be carefully pursued in order to establish the best biofuel technologies.

6 REFERENCES

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1 Bridgwater AV, Alcala A, (2013) Blends of bio-oil and biodiesel for heat and power applications", Fuel on-line March 2013