Report on Non-Biofuel Value-Added Products

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DIBANET

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2 Value-added biomass-derived products

2.1 Resources, processes and products

The Dibanet project has focussed on production of levulinic acid for conversion to ethyl levulinate to use as a diesel fuel additive. This process results in a solid residue referred to as Acid Hydrolysis Residue or AHR. One of the objectives of the project was to consider how to valorise this AHR through conversion by fast pyrolysis into a liquid fuel known as bio-oil which can be further processed into synthetic diesel and other products. A further objective was to consider how to create an energy self sufficient process without requiring fossil fuels, so parallel work on fast pyrolysis of biomass (miscanthus and bagasse) was included for bio-oil production for conversion to heat and power for process utilities and for consideration for secondary conversion into other value added products, both fuel additives and non-fuel products. It was found the high humin levels of AHR re-inforced the refractory nature of high lignin content residue which caused the fast pyrolysis research for bio-oil production from AHR to fail. Attention then moved to thermal gasification for production of fuel gas for heat and power generation to satisfy process requirements. This proved successful. Larger scale oxygen gasification of the AHR would produce synthesis gas which can be converted into synthetic hydrocarbons, alcohols, hydrogen and ammonia, all of which have both fuel and non-fuel applications. Again some attention was paid to biomass gasification as well as AHR gasification to ensure the mail levulinic acid process was energetically self sufficient. The full range of options considered is summarised in Figure 1.

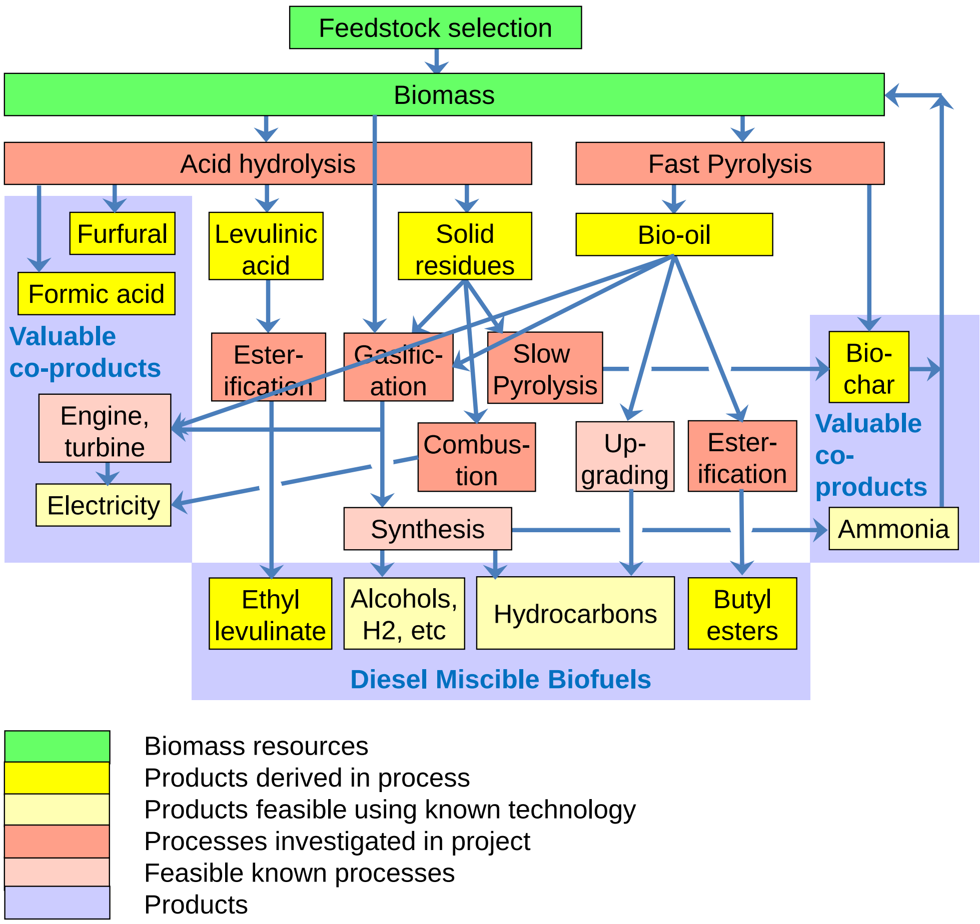

Figure 1 Biomass, processes and products

2.2 Introduction

As complete a set of relevant product prices and market sizes has been assembled from the literature for relevant products that are known to be derivable from biomass and which are currently under investigation. Table 1 lists the potential added value products from biorefineries and Table 2 lists the product price and market size for those products for which data is available. All the data is from published sources and is as recent as possible.

Table 1 Complete list of potential added value biomass derived products

Products	Route from biomass	Refs
(2,5)-bis-hydroxymethyl-furan (BHMF)	Reduction of 5-hydroxymethyl furfural or hydroxymethylation of furfuryl alcohol	1
1,2 propanediol	Hydrogenation of lactic acid	1, 3, 14
1,4-butanediol,	Carbohydrates fermentation or from succinic acid	13
2,5- dimethyl furan	Hydrogenolysis of 5 hydroxymethyl furfural	5
2-Pyrrolidone	From succinic acid	1, 13
5-aminolevulinic acid		8
Acetylene	From syngas	5
Activated carbon	From biomass pyrolysis	8
Adipic acid	From cyclohexanone or succinic acid	7, 2, 13, 16
Alkanes	From syngas by Fischer Tropsch	4
Ammonia	From producer gas	8
Benzene	From biomass gasification or catalytic hydrogenation of CO_2	10, 16
Bio-oil	Biomass pyrolysis	8
BioSyngas	Biomass gasification	6
Biphenyls	Biomass thermochemical	11
Butanediol (BD)	From fumaric/succinic acid	7, 16
Carbon fibre	From lignin	11
Carbon monoxide	Biomass gasification or catalytic hydrogenation of CO_2	10
Cyclohexane	Biomass thermochemical	11
Diesel	Fisher Tropsch synthesis (syngas)	8
Dimethyl ether (DME)	Fisher Tropsch synthesis (syngas) or catalytic hydrogenation of CO_2	2, 10
Diphenolic acid		4, 13
Ethanol	Sugars fermentation or Fisher-Tropsch synthesis	2, 3, 17
Ethyl levulinate	Esterification of levulinic acid	8
Fertiliser from bio-oil	Biomass pyrolysis	8
Fischer-Tropsch liquids	From biomass gasification	2, 13
Formic acid	Catalytic hydrogenation of CO_2	10
Furan	From furfural	1
Furan (2,5)-dicarbonic acid		8
Furan(2,5)-dicarboxylic acid (FCDA)	From 5 hydroxymethyl furfural	1
Furfural	Xylose thermal transformation	2, 3, 13
Furfuryl alcohol	Directly derived from furfural	5, 9, 13
Gasoline	Fisher Tropsch synthesis	2
Guaiacols	Biomass thermochemical	11

HMF (Hydroxymethyl Furfural)	Dehydration of hexoses (glucose, fructose)	1
Humins		5
Hydrogen	Biomass gasification	8
Kerosene	From Fisher Tropsch synthesis (syngas)	8
Levulinic acid	Sugars biochemical	2, 3, 6, 13
Linear Alpha Olefins (LAO)		7
Maleic anhydride	From succinic acid	2, 13
Malic acid	From succinic acid (sugars fermentation)	2, 3, 6, 16
Methane	Biomass gasification or catalytic hydrogenation of CO_2	10, 13
Methanol	Fisher Tropsch synthesis (syngas) or catalytic hydrogenation of CO_2	2, 10, 16
N-methyl pyrrolidone (NMP)	From succinic acid	2, 13
Paraffin waxes	Fisher Tropsch synthesis	2
Phenol	Lignin thermochemical	11, 16
Phenol formaldehyde	From biomass pyrolysis	8, 13
Phenolics	Lignin thermochemical	12
Polytetramethylene ether glycol (PTMEG)	From THF	7
Quinones	Biomass thermochemical	11
Succinate salts		17
Succinic acid	Several fermentation processes available	2, 3, 6, 13, 15
Syringaldehyde	Biomass thermochemical	11
Syringol	Biomass thermochemical	11
γ-amino levulinic acid,		17
γ-butyrolactone	Produced from glucose via succinic acid (fermentation)	7, 13
γ-valerolactone	From levulinic acid	1

2.3 References for Table 1

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Table 2 Biomass derived products, prices and market volume

Products	Market, (Tonnes/year)	Price, (Euros/Tonne)	Ref
1,2 propanediol	1,500,000	3,000	1
1,4-butanediol,	1,500,000	1,475	2
2,6 dimethoxyphenol	25,000	7,200	28
2 methyl ketone	200,000	500	28
Activated carbon	1,200,000	3,500	3
Adipic acid	2,500,000	1,150	4
Ammonia	122,000,000	460	5
Benzene	40,000,000	667	6
Carbon fibre	28,000	1,200	7
Cyclohexane	5,000,000	640	8
Diesel	~1,000,000,000	Closely linked to oil price	9
Dimethyl ether (DME)	150,000	450	10
Ethanol	4,600,000	740	11
Ethanol industrial	9,660,000	755	12
Formic acid	500,000	1,000	13
Furfural	250,000	500	14
Furfuryl alcohol	350	350	15
Gasoline	~1,000,000,000	Closely linked to oil price	9
Hydrogen	54,000,000	2,000	16
Kerosene	~1,000,000,000	Closely linked to oil price	9
Levulinic acid	450	8,000	17
Maleic anhydride	1,600,000	1,450	18
Malic acid	25,000	1,443	19
Methane	600,000,000	800	20
Methanol	40,000,000	254	21
Pentanoic acid butyl ester	500	46,000	28
Phenols	9,000,000	1,400	22
Phenol formaldehyde	2,300,000	150	23
Phenolics	9,000,000	1,400	24
Succinate salts	15,000	1,100	25
Succinic acid	45,000	5,000	26
Vanillin	12,000	12,500	28
Xylene	33,000,000	775	27

Table 3 References for Table 2 - Biomass derived products, prices and market volume

Ref.	Reference (Price)	Reference (Market Volume)
1	ICIS at www.icis.com	Report available at: http://www.projects.science.uu.nl/brew/programme.html
2	ICIS at www.icis.com	SRI Consulting at www.sriconsulting.com

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8	ICIS at www.icis.com	http://www.icis.com/v2/chemicals/9075159/benzene/uses.html
9	n/a	BP statistical review 2011 downloadable from http://www.bp.com/sectionbodycopy.do?categoryId=7500&contentId=7068481
10	http://www.bateman.co.za/TECHNOLOGY/20080715105033312.pdf. Accessed early 2010. No longer available.	http://www.brain-c-jcoal.info/cctinjapan-files/english/2_4A4.pdf
11	ICIS at www.icis.com	http://www.icrisat.org/Biopower/philippines-event/HenriBardonSupplyChainManagementMay07.pdf
12	ICIS at www.icis.com	http://www.icrisat.org/Biopower/philippines-event/HenriBardonSupplyChainManagementMay07.pdf
13	http://wcm.paprican.ca/newsevt/WCMPublicNews.nsf/Lookup/D43D499F79E3281E8525710E0078E8BA/$file/canada_natural_advantage_web_pres.pdf	http://wcm.paprican.ca/newsevt/WCMPublicNews.nsf/Lookup/D43D499F79E3281E8525710E0078E8BA/$file/canada_natural_advantage_web_pres.pdf
14	http://www3.interscience.wiley.com/cgi-bin/fulltext/121408263/PDFSTART	http://www.biorefinery.nl/fileadmin/biorefinery/docs/bioref/bioref0603.pdf
15	http://www3.interscience.wiley.com/cgi-bin/fulltext/121408263/PDFSTART	http://www.biorefinery.nl/fileadmin/biorefinery/docs/bioref/bioref0603.pdf
16	http://en.wikipedia.org/wiki/Hydrogen_economy	http://www.gkss.de/imperia/md/content/gkss/institut_fuer_werkstoffforschung/wtn/h2-speicher/funchy/funchy-2007/5_linde_wawrzinek_funchy-2007.pdf
17	Report available at: http://www.projects.science.uu.nl/brew/programme.html	Report available at: http://www.projects.science.uu.nl/brew/programme.html
18	ICIS at www.icis.com	http://www.osti.gov/bridge/purl.cover.jsp;jsessionid=2AFE2ADF73627D538C316A5A53477BCC?purl=/901298-nfysa5/
19	ICIS at www.icis.com	Report available at: http://www.projects.science.uu.nl/brew/programme.html
20	www.physorg.com/news9792.html	http://www.biorefinery.nl/fileadmin/biorefinery/docs/bioref/bioref0603.pdf
21	ICIS at www.icis.com	http://www.celanese.com/databook_2003-corporate.pdf
22	ICIS at www.icis.com	http://technologyconference.kbr.com/2009/Dubai/Conference-Downloads/KBR-Phenol-Leading-the-Industry.pdf
23	http://www.biorefinery.nl/fileadmin/biorefinery/docs/bioref/bioref0603.pdf	http://www.4fcrops.eu/pdf/Bologna/CHIMAR.pdf
24	ICIS at www.icis.com	http://technologyconference.kbr.com/2009/Dubai/Conference-Downloads/KBR-Phenol-Leading-the-Industry.pdf
25	http://www.springerlink.com/content/q8k1778qt	http://www.springerlink.com/content/q8k1778qt6ll45

	6ll4582/fulltext.pdf	82/fulltext.pdf
26	www.bio-amber.com	www.bio-amber.com
27	http://petrofed.winwinhosting.net/upload/6march.pdf	http://petrofed.winwinhosting.net/upload/6march.pdf
28	http://www.alibaba.com/	Estimated from http://www.alibaba.com/

3 Market analysis

3.1 Crude oil

There are well known relationships between commodity fuel prices and crude oil price – for example gasoline and diesel at the pump, tax free, is approximately 1.5 times crude oil price while heavy fuel oil is approximately 0.85 times crude oil price ([1]). The multiplier is correspondingly less at intermediate points in the supply chain. Almost all commodity fuels and chemicals are directly related to the price of crude oil by multipliers that reflect the feedstock (crude oil) and capital investment. The very large petrochemical plants around the world have to employ economies of scale in order to compete and in order to provide sufficient margin for market upturns and downturns.

3.2 Relationship between price and market

As products become more specialised and plants correspondingly smaller, feedstock costs becomes a less significant proportion of the total production cost and operating costs and diseconomies of scale become more important. This gives rise to the well known relationship between market size and product cost shown in Figure 1 ([2]). If the main outliers are removed, the relationship is shown in Figure 3. This can be useful for indicating a price band for new products, although the market size still needs to be estimated.

The figure distinguishes products as commodity, specialty, fine and polymers and plastics based on the market and price. Commodity products are the products which have a market price in the order of thousand and are produced more than ten thousand tons in volumes. Specialty products are the ones which have the market in the order of a thousand tons and priced above ten thousand Euros. Fine products have the lowest market volume ranging from one tonne to thousand tonnes and always priced above ten thousand Euros. Polymers and plastics form a continuous product spectrum in between the specialty and commodity products.

It is difficult to forecast future market size of any commodity as it is dependent on a wide range of political, environmental, financial, technological and social issues according to the product concerned. Many predictions of future markets for commodities are based on a no-change scenario, due to the impossibility of satisfactory forecasting. This applies especially to crude oil prices which are subject to considerable changes from relatively small changes in political environments. Both short and long term price prediction of crude oil is not only difficult but subject to long and deep debates due to its importance in the world economy. Crude oil prices are important due to so many commodities being derived from crude oil

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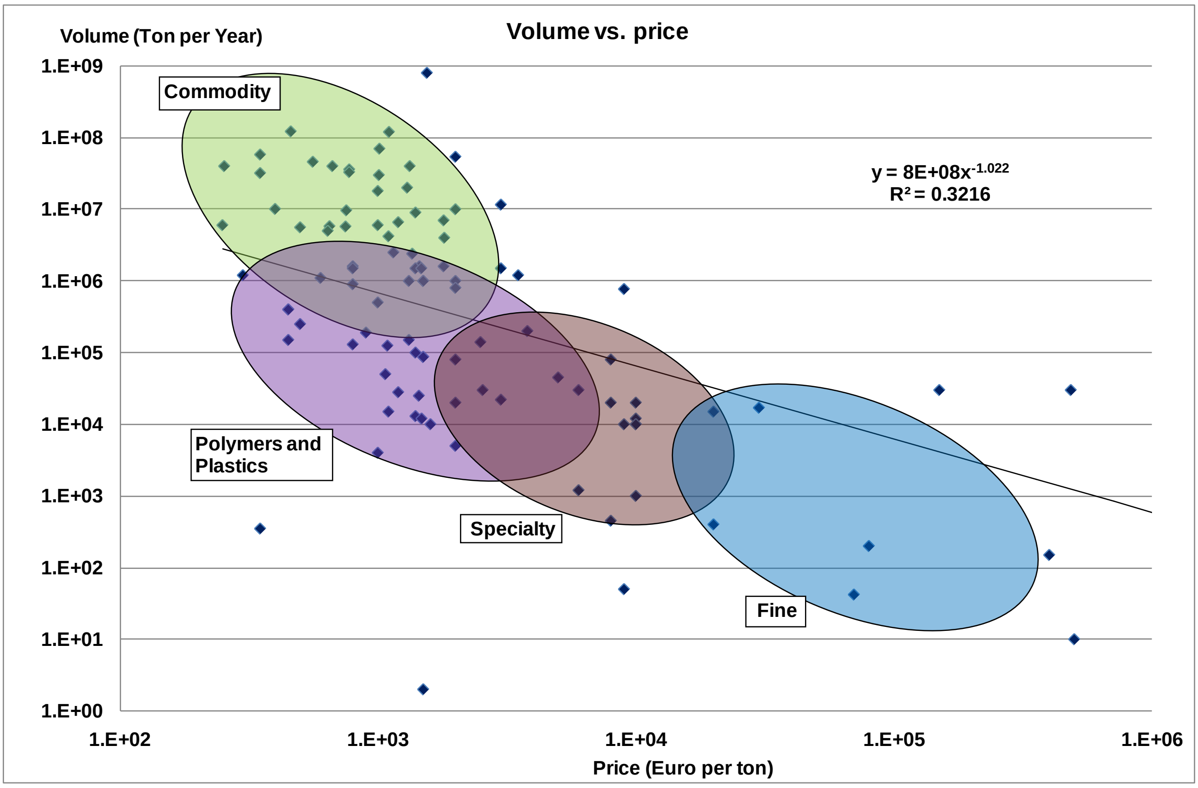

Figure 2 Biomass derived products, market volume vs. price

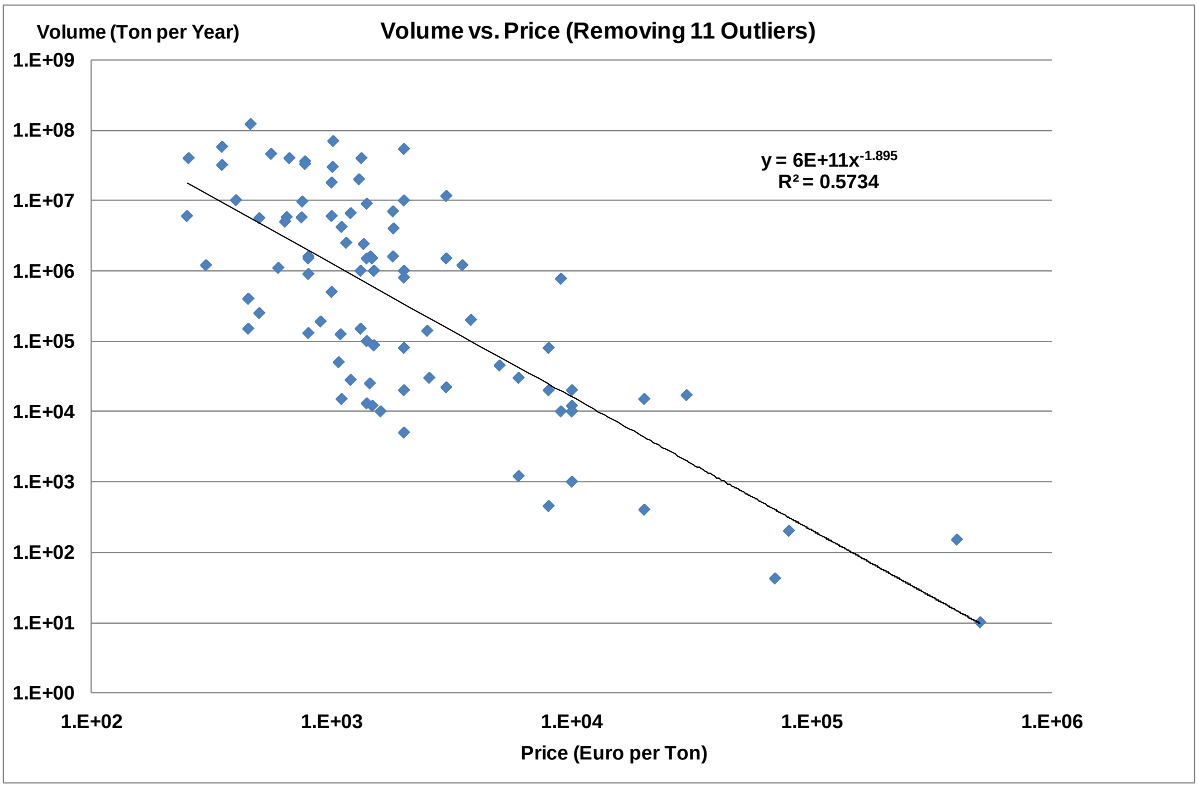

Figure 3 Biomass derived products, Market volume vs. Price (removing outliers)

3.3 Prices

There are many influences on price including:

- Most commodity prices are based on crude oil and gas prices, neither of which can be predicted with any confidence as the past few years have shown as illustrated above. Some of the more basic commodities can be directly related to crude oil prices such as gasoline which is reliably constant at around 1.5 to 1.6 times crude oil price.
- Supply and demand relationships can have substantial impact on prices when small changes in availability of commodities can have a disproportionate effect on price. For example a 5% reduction in availability can result in a 50 to 100% increase in price. This is seen for many products including crude oil and is particularly significant for commodities where supply matches demand.
- Competition between companies and between technologies can result in short term reductions.
- There can be substantial differences between contract prices and spot prices. Contract prices tend to lag spot prices by between ½ and 2 years depending on the chemical and conventional practice for that industry.
- Fiscal incentives can distort market prices and volumes as evidenced in may renewable fuels and bioenergy prices.
- Learning effects have been shown to give a long term deflation effect on prices with real terms prices dropping by between 15 and 35% for every doubling of cumulative production.

4 Products

4.1 Products

The products being produced within the experimental programme in Dibanet are:

- Levulinic acid
- Ethyl levulinate
- Formic acid
- Furfural
- Bio-oil
- Butyl esters of bio-oil
- Biochar

The products that are potentially derivable are:

- Fuel gas
- Electricity
- Ammonia
- Methanol
- Mixed alcohols
- Ethanol
- Hydrocarbons for refining to diesel, gasoline and kerosene
- Aromatics for refining to gasoline, benzene, toluene, xylene
- Hydrogen

All of these and the outline process routes are summarised in Figure 1.

There are many secondary and tertiary products possible from the products listed above and reviewed in the assessment. Especially in considering thermal gasification, any conventional organic chemicals are feasible, although they may not be economic.

4.2 Acid Hydrolysis Residues

As the process modelling of the levulinic acid production moves to completion, it is clear that there is far more AHR likely to be available that initially considered. For a the nominated 500,000 t/y dry biomass input, it is estimated that there will be around 350,000 dry t/y solid residue. This would generate around 80 MWe of electricity plus around 110 MWth of heat using either gasification and a gas turbine, or combustion and a Rankine cycle. A considerable export of electricity would thus be possible. Alternatively if all the residue is gasified to syngas, the surplus after generating all the process power requirements could be used to synthesise hydrocarbons, alcohols or ammonia. The choice depends on the economics and markets, although at this scale, the product costs would be very high, probably unacceptably high.

4.3 Levulinic acid and esters and alternative DMBs

The predicted yield of levulinic acid is around 15wt.% on dry biomass. This requires esterification to ethyl levulinate. There is however a substantial solid residue which could in principle give an additional 14 wt.% hydrocarbons through gasification and Fischer Tropsch synthesis, although the scale is very small. Thus a total biofuel yield of 29wt% seems possible

An alternative for a diesel miscible biofuel is butyl esters from bio-oil esterification, also at around 15 wt.% on dry biomass. There is a residue from esterification which by the same argument might be gasified for Fischer Tropsch synthesis to give an additional 12wt.% hydrocarbons but the scale is very small. A total biofuel yield of 27 wt.% seems possible.

For comparison, hydrotreating bio-oil from fast pyrolysis is estimated to yield around 17wt.% crude hydrocarbons on a dry biomass basis which require upgrading to give a diesel miscible fuel, possibly reducing yield by 2 wt.% to around 15 wt.%. This includes provision for production of hydrogen.

Aromatisation of fast pyrolysis vapours over zeolite catalysts is estimated to give 18-20 wt.% aromatics which are easier to use directly than hydrotreated bio-oil. They can also be used in the aromatic chemicals sector, which is one of the big five global chemical sectors.

Fischer Tropsch synthesis of hydrocarbons from biomass yields around 20wt.% hydrocarbons based on large operation and substantial development and down scaling.