

A PRELIMINARY REPORT
Some Key Features of Biofuels
FROM THE PYROLYSIS AND BIOREFINERY OF BIOMASS

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Some Key Features of Biofuels from the Pyrolysis and Biorefinery of Biomass – A Preliminary Report

I. Introduction

This project aims to demonstrate a low emission biofuel technology for the production of high quality liquid fuels and biochar from the pyrolysis of biomass and the subsequent biorefinery of the bio-oil. There is currently a lack of understanding about the properties of such biofuels (*not to be confused with biodiesels*) from the pyrolysis-biorefinery of lignocellulosic biomass. Therefore, a significant roadblock in the establishment of an Australian biofuel industry is the lack of confidence, which does not favour commercial investment in this area.

This report aims to demonstrate some basic characteristics of biofuels, which are fundamentally different from the liquid fuels that are produced from the refinery of petroleum.

II. The Need for Biorefinery and Product Engineering

Figure 1 shows the concept of Renergi's advanced biofuel technology. The technology consists of two steps. The first step is the pyrolysis of biomass to produce bio-oil (also termed as green crude or green bio-crude) and biochar. The pyrolysers will be small in scale and distributed in the region where biomass such as mallee is grown. The use of modular pyrolysers effectively reduces the need to transport wet bulky biomass over long distances. This is an important feature contributing to the economic competitiveness of Renergi's technology.

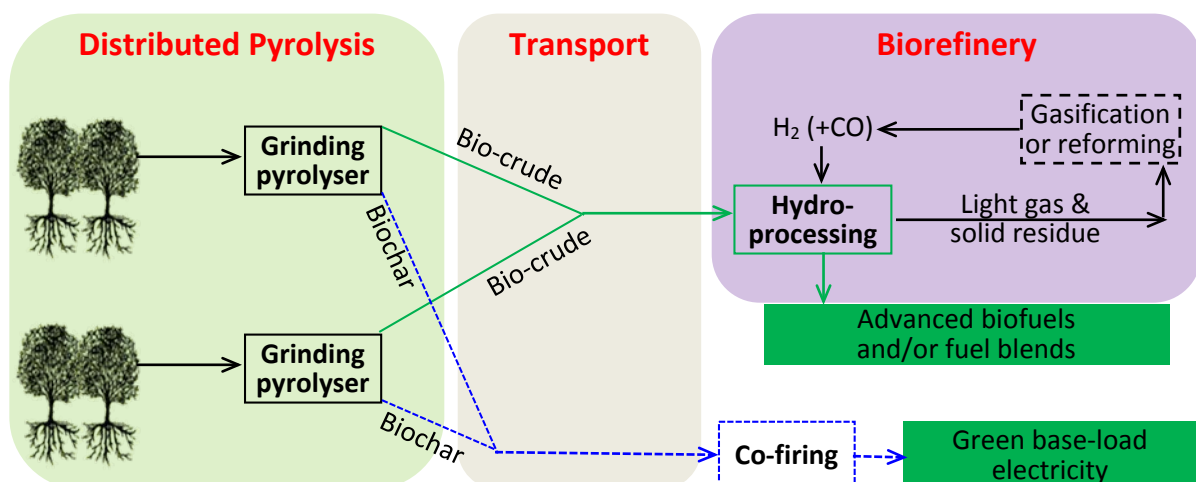


Figure 1. A schematic diagram showing the concept of Renergi's versatile advanced biofuel technology. There are many possible commercial routes for the utilisation of biochar: only one route is shown here.

The second step of Renergi's technology is to collect the green bio-crude for further refining in a biorefinery to produce high quality transport biofuels. The biorefinery step is essential because bio-oil cannot be used directly in vehicles. This is because bio-oil is a mixture of a wide variety of chemical compounds with abundant oxygen-containing functionalities. Some inorganic species in biomass (e.g. K) can also be volatilised during pyrolysis and condensed into bio-oil. Some key characteristics of bio-oil dictate the need for its refinery:

A. Bio-oil is highly polar, acidic/corrosive and unstable. For example, a bio-oil could contain up to 8 wt% carboxylic (mainly acetic) acids, making bio-oil very acidic with a pH of 2-3. In addition to acids, bio-oil also contains very reactive/unstable structures such as aldehydes (even hydroxyl aldehydes) and sugar. They are largely responsible for the formation of deposit during bio-oil storage and contribute significantly to the formation of coke during biorefinery.

It should be emphasised that not all O-containing structures in the biorefinery products will present a problem to the fuel quality. In fact, the presence of some oxygen in stable structures in liquid fuels could be beneficial in ensuring a smooth combustion in internal combustion engines to reduce the emissions of air pollutants such as particulates (black smoke). In the long term, there must also be a change in fuel standards for the emerging biofuel industry.

B. Bio-oil contains heavy species. Biomass is mainly made of natural polymers such as cellulose, hemicellulose and lignin. Pyrolysis partially disintegrates these polymers to produce molecules of a wide range of molecular sizes, including large polymeric/oligomeric molecules from the partial breakdown of these natural polymers. These polymers make bio-oil highly viscous. However, these polymeric/oligomeric molecules are not the simple fragments of cellulose, hemicellulose and lignin because other reactions have also taken place during the thermal breakdown of the natural polymers in biomass. For example, while lignin itself in wood contains little large aromatic ring systems (e.g. having > 3 fused benzene rings), the lignin-derived oligomers in bio-oil contain significant amounts of large aromatic ring systems.

These polymeric/oligomeric molecules in bio-oil would be rich in oxygen in abundant O-containing functional groups.

C. Bio-oil contains water and has low heating values. The moisture in the biomass feedstock for pyrolysis is condensed into the bio-oil. Additional water is produced during pyrolysis. Bio-oil also has high contents of oxygen, which has originated from the oxygen-containing structures in biomass feedstock for pyrolysis. Therefore, bio-oil has lower heating values than petrol or diesel from the refinery of petroleum. A large fraction of oxygen in bio-oil needs to be removed through a variety of reactions during biorefinery.

The most important process of biorefinery is hydrotreatment, as is shown in Figure 1. In this report, the products from hydrotreatment are termed as biofuels.

III. Some Key Features of Biofuels

III.1. Bio-oil and its hydrotreatment

Mallee wood was pyrolysed to produce bio-oil samples in a pilot plant purposely built based on our grinding pyrolysis technology.

The bio-oil sample was then hydrotreated under a wide range of experimental conditions to produce biofuel samples. Depending on the hydrotreatment conditions, the bio-oil may be hydrotreated to various extents, yielding products ranging in colour from almost colourless to dark brown.

III.2. GC-MS analysis

Gas chromatography – mass spectrometry (GC-MS) was used to analyse the composition of biofuels. Some typical total ion chromatograms of biofuel samples are shown in Figure 2 together with those of commercial petrol and diesel obtained from a petrol station in Perth.

The sharp contrast between biofuels and petrol/diesel can be clearly seen in Figure 2. As is well known, petrol and diesel are featured by straight-chain aliphatic hydrocarbons. For example, the diesel (Figure 2) contains C₁₀ to C₂₅ hydrocarbons. The GC-MS instrument for the analysis was not configured to analyse the light components. Very light/volatile components, especially those in petrol, are thus not shown.

However, these long chain (C₁₀ to C₂₅) aliphatic hydrocarbons are almost absent in the biofuel samples in Figure 2 that have originated from mallee wood. Although the biofuel samples did show some light straight-chain (especially C₄, C₅, C₆ and C₈) hydrocarbons (not shown), it is believed that they have originated from the hydrotreating reactions. The biofuels from other types of biomass feedstocks with waxes (e.g. leaves) might contain a bit more straight-chain aliphatics, but will not be the dominant components.

Table 1 show the identification of the main components in the biofuel samples shown in Figure 2. There are significant amounts of (substituted) cyclic hydrocarbons in the biofuels, especially in well-hydrotreated biofuel samples.

Biofuels also contain aromatics. Substituted benzenes are particularly abundant. The most abundant oxygen-containing functional group is the phenolic group in the less hydrotreated biofuels.

III.3. Simulated distillation

The simulated distillation was carried out following the ASTM D2887 method. Figure 3 shows the simulated distillation chromatograms of some biofuel samples. For comparison, the corresponding chromatograms of the petrol and diesel samples are also shown.

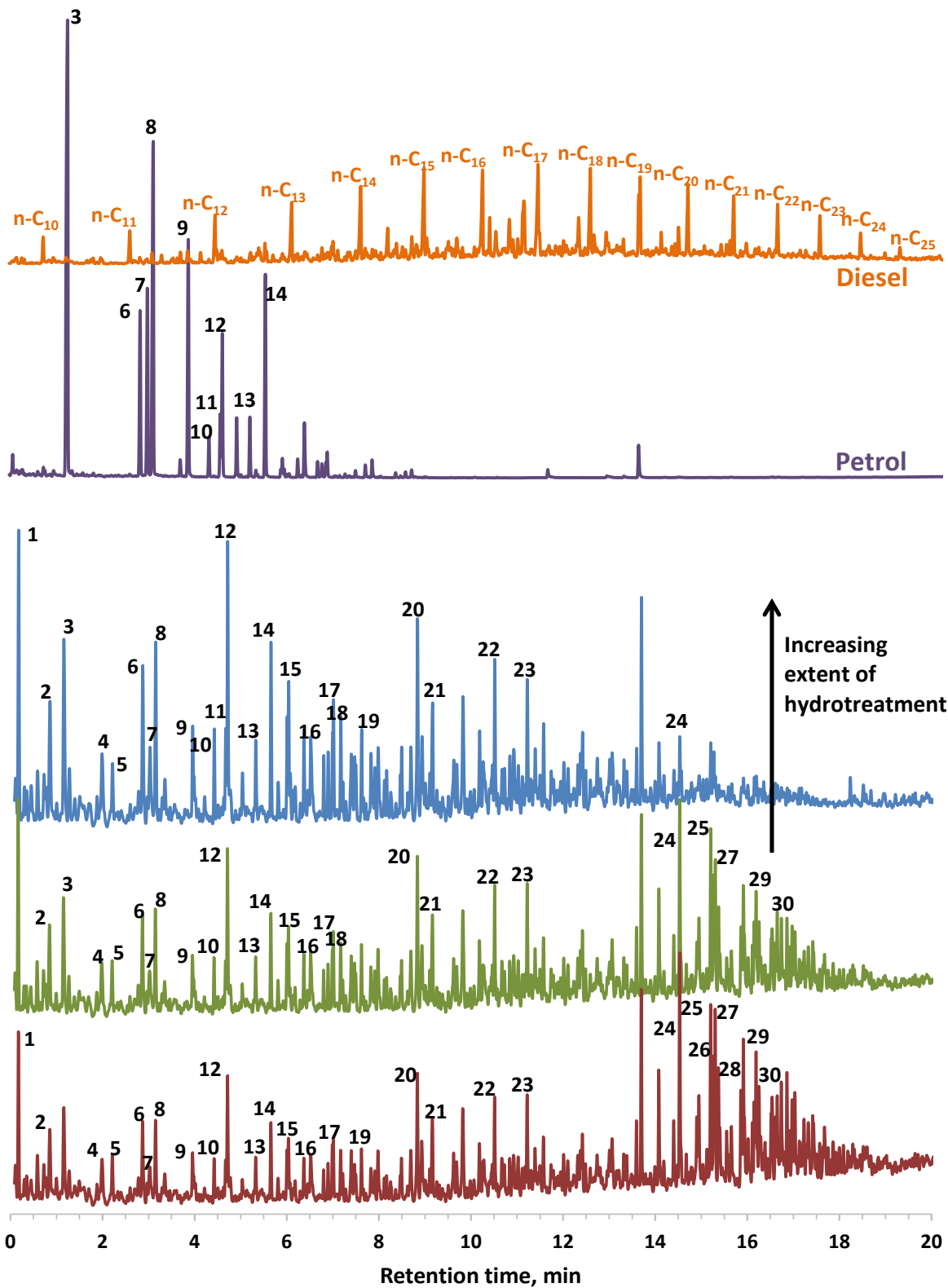


Figure 2. GC-MS chromatograms of biofuels produced from the varying extents of hydrotreatment. Those of commercial petrol and diesel are also shown for comparison. Note that the GC-MS instrument was configured to operate under the conditions aimed at the heavier components and that the lighter components are not shown.

Table 1. Identification of the compounds labelled in Figure 2.

Peak No	Compound	Peak No	Compound
1	Propylcyclohexane	16	1-Propyl-2-methylbenzene
2	1-Methyl-2-propylcyclohexane	17	Indane
3	Toluene	18	1-Methyl-4(1-methylpropyl)benzene
4	Butylcyclohexane	19	1,4-Diethylbenzene
5	Octahydro-1H-Indene	20	2,3-Dihydro-4-methyl-1H-Indene
6	Ethylbenzene	21	1,2,3,4-Tetrahydronaphthalene
7	p-Xylene	22	1,2,3,4-Tetrahydro-5-methylnaphthalene
8	m-Xylene	23	1,2,3,4-Tetrahydro-6-methylnaphthalene
9	o-Xylene	24	o-Cresol
10	Propylbenzene	25	2-Ethylphenol
11	1-Ethyl-4-methylbenzene	26	3,6-Dimethylphenol
12	1-Ethyl-3-methylbenzene	27	p-Cresol
13	1-Ethyl-2-methylbenzene	28	m-Cresol
14	1,2,3-Trimethylbenzene	29	4-Ethylphenol
15	1-Propyl-4-methylbenzene	30	3-Ethylphenol

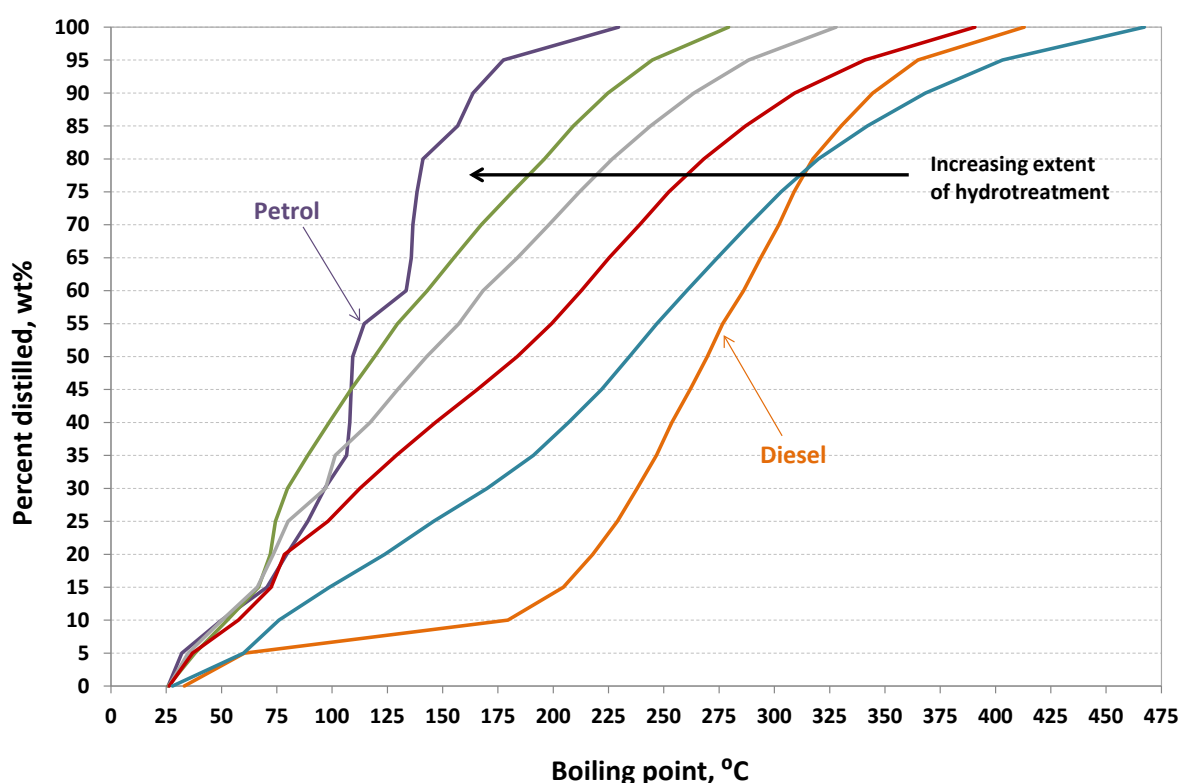


Figure 3. Simulated distillation chromatograms of biofuels produced from the varying extents of hydrotreatment. Those of commercial petrol and diesel are also shown for comparison.

The data in Figure 3 clearly show that the hydrotreatment of bio-oil can produce biofuels in the boiling point ranges for petrol and diesel. As is in the case of the existing petroleum refinery, distillation will be required to separate (cut) the hydrotreatment product into various commercial products. Again, as is in the case of the existing petroleum refinery, blending may also be required in commercial operation to give fuel products of special properties.

III.4. Density

The biofuels could have a density mainly in the range of 780 to 920 kg/m³ depending on the extent of hydrotreatment. This density range appears to be somewhat higher than those specified in the Australian fuel standards: 820 to 850 kg/m³ for diesel.

However, it should be noted that the reasons, and thus possible concerns, for high density are different for diesel and biofuels. A major reason for limiting the diesel density to be <860 (after 1 Jan 2002) or <850 kg/m³ (after 1 January 2006) is to limit the contents of polyaromatics and other heavy species, which, among other negative impacts, could cause/enhance the formation of black smoke (particulates) during the combustion in an engine. However, a significant contributor to the density of biofuels is their contents of oxygen-containing functional groups. It is hypothesised that oxygen-containing structures in biofuels could help to smooth the combustion in an engine, which will in turn help to reduce the formation of smoke (particulates). This hypothesis will be verified in the future.

IV. Conclusions

Some biofuels from the hydrotreatment of bio-oil have been characterised. The preliminary data indicate that biofuels have a fundamentally different composition from the current petrol and diesel produced from the refinery of petroleum. Future work will investigate the behaviour of biofuels in practical engines. This will provide useful information for the formulation of future fuel standards encouraging the market penetration of biofuels.