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Feeding Biomass into a Mineral Oil Refinery
Process Routes and Feedstock Preparation

Technical paper

Ligno-cellulosic biomass such as agricultural and forestry waste streams can be converted decentralized into pyrolysis oils and transport to a mineral oil refinery for co-refining to biomass derived liquid transportation fuel components. Due to the different composition of pyrolysis oil compared to mineral oils (such as a much higher oxygen content) direct co-refining by simple mixing is not recommended. It is shown that mild hydrotreating produces a feedstock that can be mixed with the regular cat cracker feed up to 20%. The resulting liquid product, after cracking of the mixture in a FCC-unit facility of Shell, is free of oxygen probably due to hydrogen transfer from the mineral oil. The product slate is essentially the same as for the mineral oil only. The required hydrogen could also be produced from the pyrolysis oil (e. g. by gasification). It is shown here that hydrogen or synthesis gas (e. g. for alcohol or Fischer-Tropsch fuels) can preferably be produced by catalytic steam reforming of pyrolysis oil in a special reactor unit, in the form of a stand alone unit or in combination with an existing reformer (e. g. running on refinery gas).

Key words: *co-refining biomass, pyrolysis oil, blending components, steam reforming, FCC of pyrolysis oil, hydrotreating, oxygen removal, hydrogen transfer, gasification*

Introduction

The production of liquid transportation fuels (blending components) from biomass is of growing importance. Fossil fuels are not sustainable and the increasing concern on the CO_2 and other greenhouse gas emissions and on the availability and price of crude oil makes biomass an interesting base source of transportation fuels. In principle, the use of biomass would avoid CO_2 emission from fossil origin and the quantities of biomass available should be sufficient for an important contribution to the liquid transport fuel pool. To increase the amount of biomass derived transportation fuels the recent EC guidelines now demands 10% renewables in 2020.

Present contributions (called first generation fuels) are based on biomass sources which are in principle in competition for food and feed. These fuels are mainly al-

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cohols obtained from fermentation of sugars and corn (maize) that are used in gasoline blends, and converted vegetable oils from seeds or animal fats meant to be blended with diesel. Conversion processes for these diesel blends are trans-estherification to produce FAME or FAEE or hydrogenation and mild hydrocracking to produce alkanes.

While these products find widespread use, the quantities on a world scale are restricted and the moral issue of food and feed competition will limit extension of their use.

A much larger source of biomass are lignocellulosic streams of agricultural and forestry waste and potentially, dedicated fast growing energy crops.

After fractionation the cellulose and hemicellulose can be converted into sugars by enzymatic conversion (see *e. g.* IOGEN) and these sugars are suitable for conversion to alcohols while the lignin (up to 35% of the feedstock) can be used for energy generation or other products. These processes are under development worldwide and challenges are *a. o.* cost of the enzymes.

Alternative thermo-chemical routes for lignocellulosic biomass to transport fuel blends are under development too. An overview of possible thermo-chemical routes to transportation fuels is presented in fig. 1, while tab. 1 shows the different blending components aimed for in these routes.
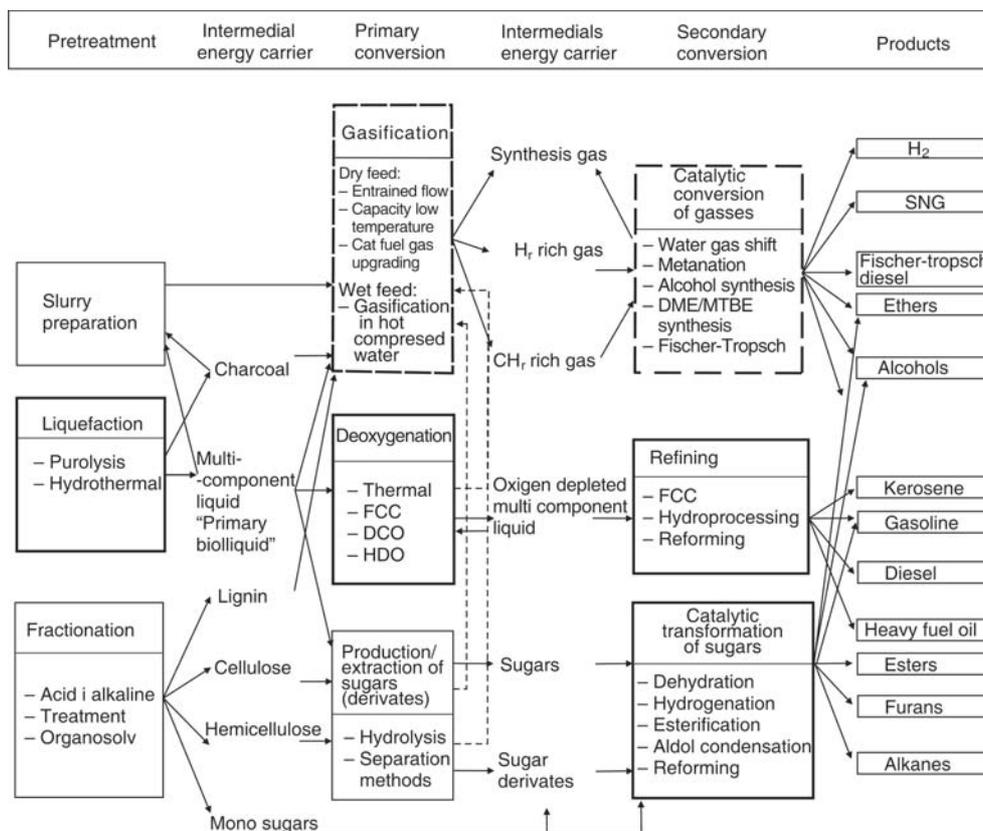

Figure 1. Thermochemical routes to transportation fuels

Table 1. Different blending components from biomass

Fossil fuel	Biomass alternative
	(100% biomass-based replacement and/or blending component for fossil fuel)
Gasoline	Alcohols (C_1 to C_4)
	MTHF (methyltetrahydrofuran)
	MTBE (methyltertiarybutylether)
	Aromatics
	Alkanes
	Levulinic acid esters
	Deoxygenated and refined primary bioliquids
Diesel	Levulinic acid esters
	Levulinic acid dimmer esters
	5-HMF (5-hydroxymethylfurfural) esters
	Alkanes
	DME (dimethyl ether)
	Ethanol
	FAEE (fatty acid ethyl esters)
	FAME (fatty acid methyl esters)
	Fischer-Tropsch liquids (from biomass-based synthesis gas)
	Deoxygenated and refined primary bioliquids
Kerosene	Fischer-Tropsch liquids (from biomass-based synthesis gas)
	Alkanes (from vegetable oils or animal fats by Centia process)

An important issue is the scale of operation of biomass conversion plants. In the fossil liquid fuel production the scale of operation is large to very large (*e. g.* 10^6-10^7 tons per year) which is advantageous because of the economy of scale but in the case of biomass this size would also involves a logistic problem. In contrast to crude oil, biomass is produced in a distributed way and generally requires extensive solids handling.

Our present contribution will concentrate on (decentralized) liquefaction of biomass and subsequent co-processing of the liquid bio-intermediates in a regular fossil fuel refinery [1].

This scheme has the advantage of the overall large scale of operation, possible lower investment due to the utilization of existing equipment, robustness for fluctuating prices and availability of biomass and crude oil and it would profit from existing storage, blending and retailer distribution systems.

For an oil refinery a liquid feedstock would be most convenient as the conventional refinery equipment is based on fluids rather than solids.

Liquefaction can be done in an extension of the refinery but from a logistics point of view and also for mineral retainment, liquefaction close to the biomass production area may be preferred.

Liquefaction

We will consider here only non catalytic fast pyrolysis. Other liquefaction processes have been development and tested in the past [2, 3] but these require slurries under high pressure while fast pyrolysis is a relatively simple atmospheric process which has reached demonstration scale.

At present several attempts are made to improve the fast pyrolysis process by catalysis [4], Ritter [5] and the BCC process of BIOeCON/KiOR/Petrobras [6] but here only the non-catalytic process will be discussed.

Fast pyrolysis is typically carried out at ~500 °C, 0.1-1 bar and with a moisture content of 10-20 W% at the reactor entrance. After condensation of the vapors a liquid is produced (up to 70%) called pyrolysis oil. Next to the oil product fuel gas and char is produced, usually partially required to energize the process.

Typical oil composition compared to heavy fuel oil is given in tab. 2. Excellent reviews on research, technology and application are available [7, 8].

Fast pyrolysis is slowly entering commercial operation. BTG (the Netherlands), Dynamotive (Canada), Ensyn (Canada) are operating pilot plants or demonstration plants with typical capacities of one to several tons per hour. The BTG technology involves a rotating cone mixer/reactor which was originally developed at the Twente University [9].
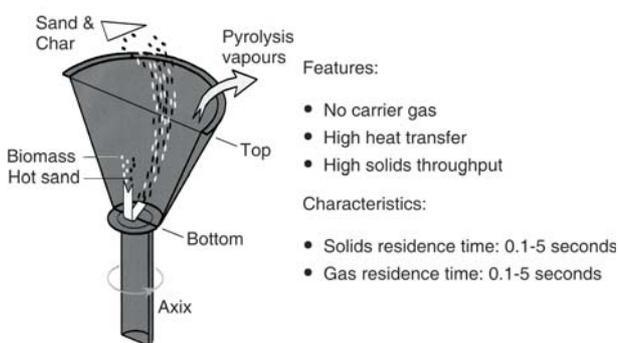

Figure 2. The rotating cone reactor

Pyrolysis oil in the refinery

As can be seen from tab. 2 pyrolysis oil differs a lot from the feed streams normally encountered in a refinery. Overall the elemental composition is still similar to the original biomass and it cannot be fed directly into the refinery units without pretreatment. Veba Oel achieved deep deoxygenation [10], with conventional catalyst Co-Mo and NiMo at 180 bar and 350-370 °C encountering many operational problems like blocking of the catalyst and considered this route less favourable. Veba subsequently used their Veba Combi Cracking Process and could deoxygenate pyrolysis oil up to 80% and successfully tested it in 15/85 blends with LCO in a FCC-Mat unit.

UOP also tested pyrolysis oil and lignin fraction in blends with 80% VGO in a lab scale FCC unit [UOP 2005, 11]. Problems encountered were increase in coke make, acidity of the pyrolysis oil and change in product slate.

Table 2. Properties of pyrolysis oil and heavy fuel oil

Characteristic	Pyrolysis oil	Heavy fuel oil
Water content [w%]	15-35	0.1
C [w%, dry]	50-64	85
H [w%, dry]	5.2-7	11.1
O [w%, dry]	35-40	1.0
N [w%, dry]	0.05-0.4	0.3
S [w%, dry]	0.05-0.3	2.3
Heating value [MJkg^{-1}] (LHV)	16.5-19	40
Viscosity (cp at ~50 °C]	40-150	180
pH	2.4	–
Total acidity number (TAN)	70-150	–
Specific gravity	1.15-1.25	0.90
MW [gmol^{-1}]	600-700	180-400

Our group was involved in BIOCOUP, an integrated project in the sixth frame-work program of the EU, together with key partners Shell, Arkema, Albemarle, VTT (Finland), University of Groningen (the Netherlands), BTG (the Netherlands), CNRS (France) and Boreskov Institute of Catalysis (Russia). In Twente we tested [12] a limited degree of hydrogenation to produce an oil (called HDO oil) from the whole pyrolysis oil (or fractions of it).
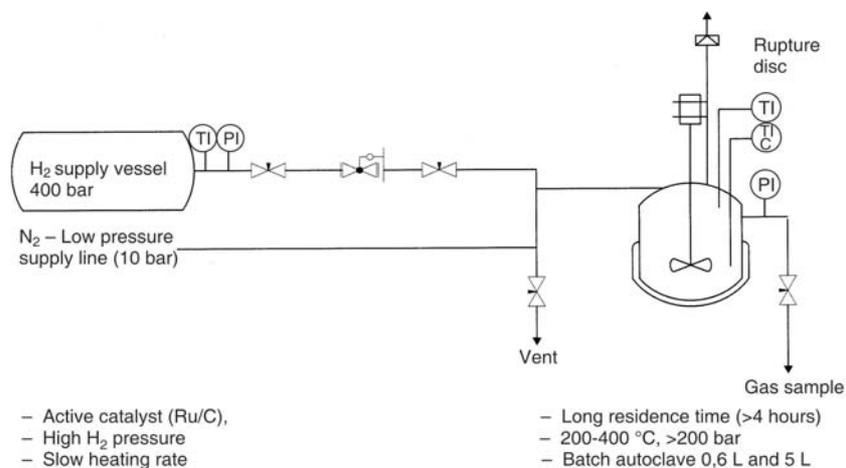

Figure 3. Hydrodeoxygenation (HDO), experimental set-up

Lab-scale batch tests at different conditions, see fig. 3, with the whole pyrolysis oil produced HDO oils, which depending on temperature contained 28-16% oxygen compared to 39% in the dry feed oil (see tab. 3). The HDO oils produced were converted by Shell in their FCC-mat facilities. Mixed with long residue in a 20/80 ratio, product slates and gasoline yield were not much different from the long residue only and no plugging etc. occurred while nearly all oxygen was removed (see fig. 4). Undiluted HDO oil however produced, depending on hydrogenation temperature, more coke ~37-22% and less gasoline ~22-35%.

Table 3. Oil properties and H_2 consumption for whole pyrolysis oil

	Feed oil	HDO oils	Gasoline*
C dry [wt.%]	54	63-74	86-89
H dry [wt.%]	7	9-10	14-11
O dry [wt.%]	39	28-16	0
Water [wt.%]	25	16-2	0
HHV [MJkg^{-1}]	17	25-35	~46
Coking tendency [dry MCRT, wt.%]	27	14-2	~0

*	Temperature [°]	230	260	300	330	340
	NL H_2/kg feed oil	232	237	290	297	326
	NL H_2/MJ of product	21.6	22.0	22.3	21.8	23.6

Careful analysis of the results of FCC-MAT conversion of undiluted and long residue diluted HDO oil showed an important beneficial effect of the co-processing both
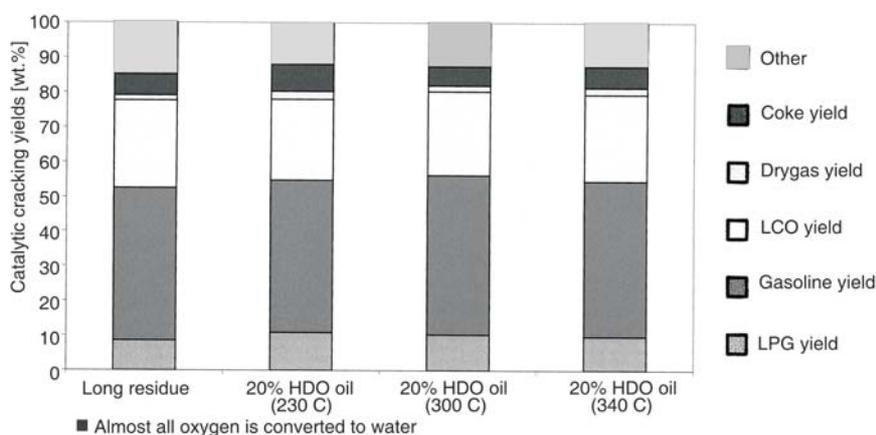

Figure 4. A co-refining product yields; HDO oil from whole pyrolysis oil

in the production of gasoline and light cycle oil (diesel precursor) which was ascribed to hydrogen transfer reactions from the fossil feed to the HDO components [12].

Syngas and hydrogen production

For the feed preparation and processing of pyrolysis oil in a refinery environment hydrogen will be required and this can also be produced from biomass via syn(thesis)gas ($CO + H_2$) production and the water gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$). Moreover syngas could be used to produce alcohols for fuel blending components or for the synthesis of Fischer-Tropsch fuels.

Synthesis gas can be obtained from carbon containing solid fuels like coals or coke via gasification with oxygen and steam. For the gasification of coal, nowadays entrained flow reactors (see fig. 5 for a reactor overview) are applied operating at very high temperatures and scale of operation [13]. Because of the smaller scale of operation and the more reactive feed for biomass usually low temperature gasification (<1000 °C) is preferred and often the use of pure oxygen is circumvented by creating different zones (*e. g.* double fluid or entrained beds) (see also the Gussing gasification plant).
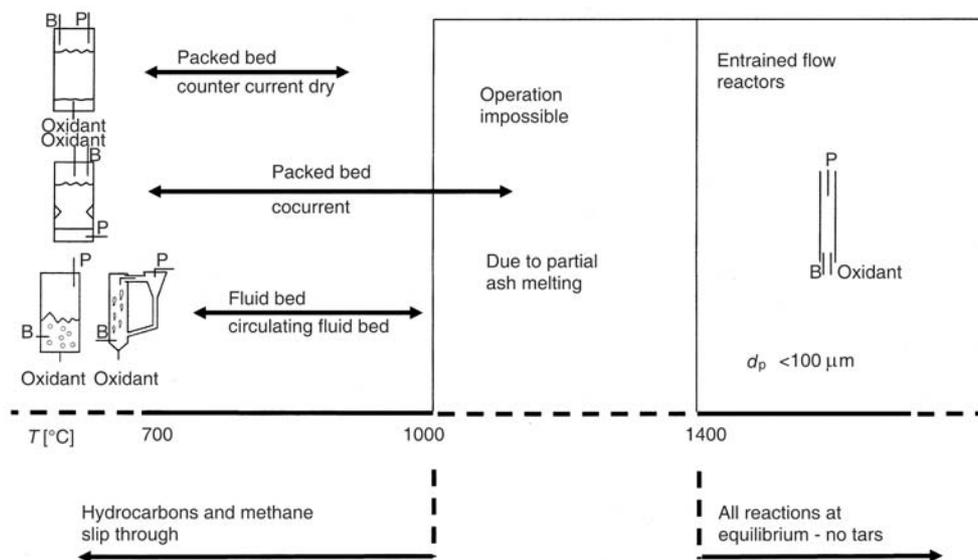

Figure 5. Gasification of solids; types of reactors for different temperatures

This low temperature gasification comes however at the cost of extensive gas cleaning (tars *etc.*) and incomplete conversion to syngas (CH_4 containing gas). If a refinery has (heavy residue) oil gasifiers pyrolysis oil or fractions of these could be co-fired in these units to produce syngas of hydrogen. Pyrolysis oil could also possibly be converted to syngas and/or hydrogen via steam reforming [14]:

$$C_6H_{10}O_4 + 2H_2O \;\rightarrow\; 6CO + 7H_2$$
(Catalyst) 600-900 °C
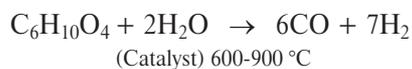
In our group this concept was developed as a two step staged process [15] and studied on pilot scale (see fig. 6).
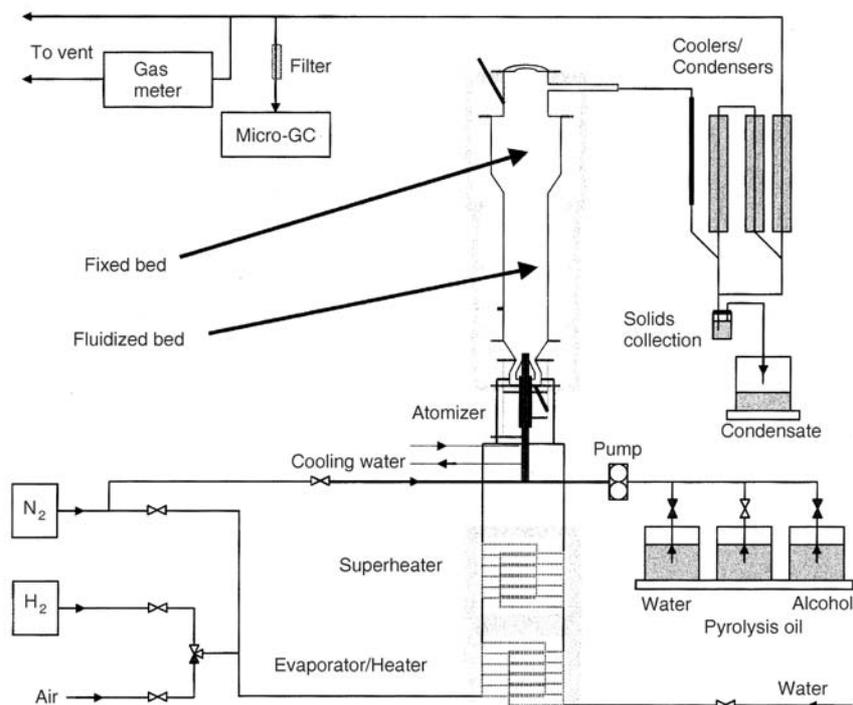

Figure 6. Two stage reform process flow diagram; Experimental set-up

The pyrolysis oil is atomized and blown into a fluid bed and converted into vapors and a small amount of coke (to be used in a combustion process to provide heat). The vapors pass through a fixed bed with a commercial reforming catalyst, fig. 7, shows that an excellent synthesis gas can be produced for a prolonged period of time. Of course ultimately much longer tests are required for long duration testing of the system. It is however interesting to note that in an existing reformer (*e. g.* of methane or refinery gas) pyrolysis oil could be fed in via the atomizer/evaporator under a large excess of steam (say steam/carbon >15) passing through a pre-former bed before the product stream is mixed with additional methane to reach a steam/carbon ratio of say 3 at the primary reformer for production of the bulk of the synthesis gas. In this way biomass in the form of pyrolysis oil can be co-fed to an existing reformer to produce synthesis gas or hydrogen.
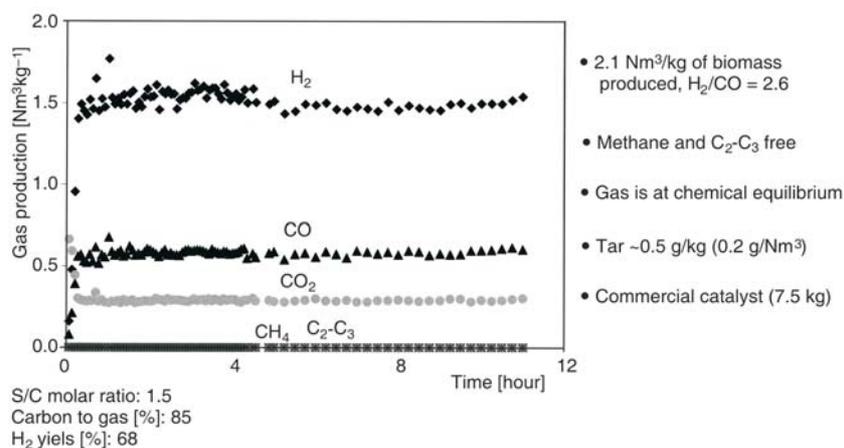
Figure 7. Two stage reforming of pyrolysis oil; results of longer duration run

Conclusions

Introduction of lignocellulosic biomass derived transportation fuel blends via co-refining in a mineral oil refinery can be an interesting option.

Pyrolysis oil can be a good starting point. Once hydrotreated to a certain degree it can be mixed with the regular cat cracker feed up to 20% and profit from the co-feeding of the mineral oil by reaching complete deoxygenation via hydrogen transfer of the mineral oil. The overall product slate can remain the same as for the original feedstock under these conditions.

Pyrolysis oil can be used as a feedstock for hydrogen and syngas production in a refinery. Apart from oil gasification it can also be applied for (co-) reforming with steam. In this way hydrogen, Fischer-Tropsch oils and alcohols can be produced (partially) based on lignocellulosic biomass.

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