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Production of high quality syncrude from lignocellulosic biomass

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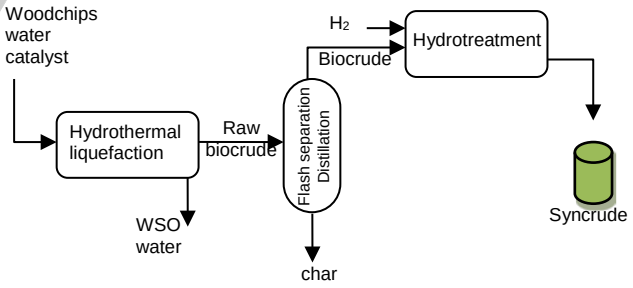
Abstract: Wood chips were hydrothermally treated in near critical point water in the presence of a catalyst to yield a raw biocrude, containing a wide range of organic components. This product was subsequently distilled to remove its heaviest fraction, which tends to yield chary products when heated above 350ºC. The biocrude obtained has an oxygen content of 12 wt% and was subsequently hydrotreated to obtain a hydrocarbon stream. Varying the hydrotreatment operating conditions and catalyst yielded a deoxygenated syncrude which quality improved with operation severity. The hydroprocessed stream produced under very mild conditions can be further upgraded in conventional refinery operations while the stream produced after more severe hydrotreatment can be mixed with conventional diesel. This proof of concept was demonstrated with commercial hydrotreating catalysts, operating between 350 and 380ºC, 40 to 120 bars pressure and 0.5 to 1 h^{-1} contact time.

Biofuels are a good replacement for petroleum-based fuels to help reduce CO_2 emissions in the transportation sector.1 First generation biofuels, based on the transformation of sugar (mainly from corn or sugarcane) into ethanol represent a useful resource. However, their greenhouse gas reduction potential as well as supply are limited. By the contrary lignocellulose transformation into fuels does not compete with food uses and this feedstock is largely available, with a resource estimated at 1 billion tonnes per year in the US alone.[2] While a number of processes have been developed, the economical transformation of lignocellulose into fuels, competitive with petroleum-based products, is still a challenge. Although enzyme-based deconstructions of lignocellulose liberate sugars that are transformed into ethanol, these processes are constrained by enzyme cost and the inherently limited yield; not all the biomass is used in these transformations.[3] Biomass gasification does use the whole biomass, but process efficiency is limited, due to moisture content, slag formation and the costly need to clean the syngas for further liquid production.[4] Among thermochemical processes that convert the whole biomass into liquid, pyrolysis is an efficient and cheap process. Yet the liquid product obtained is of too low quality (unstable, wet and acidic) for a straightforward application in transportation fuels. Pyrolysis oil upgrading through hydrotreatment has proved to be challenging, requiring high operating pressure and exposed to premature deactivation of the catalyst.[5]

Hydrothermal liquefaction is another technology that uses the whole lignocellulosic biomass, with the advantage that the feedstock does not need to be dried. Indeed, the biomass is treated in an aqueous medium, near its critical point (330-380ºC, 200-300 bar), and is broken apart yielding a liquid and some gas (essentially CO_2 with only very minor amounts of H_2, CO and CH_4). The oily fraction that can be separated from the aqueous phase is more viscous and has a higher molecular weight than pyrolysis oil, but is more stable and, most importantly, has a substantially lower oxygen content, making upgrading much easier.[6] These characteristics are also reflected in the energetic content of the oil, which was reported in the range of 30-35 MJ/kg for a wide range of organic feeds[7] as compared to pyrolysis oil, often in the range of 15-20 MJ/kg depending on the water content.[8]

We hereby report the transformation of pine woodchips (Pinus Radiata from Australia) into a high quality hydrocarbon stream with very low oxygen content, suitable for further upgrading in refinery or direct blending with diesel depending on the severity of the treatment.



Scheme 1. Simple process flow for lignocellulose to syncrude. WSO: Water Soluble Organics

While most of the research on hydrothermal treatment was performed in batch, it became necessary to develop continuous mode operations for the process to become economical.9 The sample of biocrude used in this study was taken from a 10,000 tonnes per year nameplate capacity unit developed by Licella for large scale testing of hydrothermal treatment with different fedstocks.[10] In the present case, the lignocellulose (e.g. pine woodchips) was first reduced in particle size of about 500 microns and suspended in water so that the mixture could be fed through

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the type of slurry pump being used. Larger particles up to 2 mm diameter also were successfully been employed in the same system. The slurry was then raised to the operating reaction temperature by a combination of electrical heating, heat exchangers and supercritical steam injection. After the addition of a homogeneous base catalyst (an alkali solution) by means of a high pressure dosing pump, the slurry was pumped into a vertically oriented, serpentine tubular reactor.[11] Operating conditions were maintained slightly below the critical point of water, in the 330-350ºC temperature range and 200-250 bar.[12] The residence time in the reactor was typically around 20-30 minutes, after which the initial slurry was transformed into an oil-water emulsion which also contained a small amount of solid material, i.e. mostly ash from the feedstock. At the reactor output of the high-pressure reactor this stream is partially cooled and then directly flashed, splitting the emulsion and ensuring a rapid and efficient separation between oily products and an aqueous phase. This aqueous phase carries the catalyst and a number of water-soluble organics, among them small ketones, acids and phenols that may be recovered downstream for further valorization. On a dry basis the oily phase recovered may represent about 30-35 wt% of the dry biomass fed to the hydrothermal reactor. The separated, dewatered oil was further vacuum distilled following ASTM D1160 procedure in order to remove higher boiling point components which tend to transform into char when exposed to temperature above 350ºC. They represent 15 to 30% of the ex-reactor oily phase depending on the hydrothermal processing conditions.

The oily biocrude recovered after distillation and used as feedstock in this study was further characterized. It had a density of 1.03 g/cm^3 at 70ºC and a Conradson Carbon Residue (ASTM D4530) of 1.7 wt%. Elemental analysis showed a content of oxygen around 12 wt%, a nitrogen content of 0.2 wt%, and an hydrogen to carbon (H/C) molar ratio of 1.36. Sulphur was below 0.1 wt%. As indicated above, this oil quality is much better than thermal pyrolysis oil where oxygen content can be as high as 40% with H/C molar ratios close to 1.0. The oxygen content of the present biocrude is indeed similar to that of the plant oils and fats that are commercially hydrogenated today. Simulated Distillation (SIMDIS) of this oily product was also performed. Although SIMDIS data of oxygen-containing streams cannot be compared directly with those of pure hydrocarbon streams, since the removal of oxygen will result in a shift to lower temperatures, it nevertheless gives an upper limit of the boiling point ranges in the sample. In our case this indicates that the biocrude would be at least similar to a petroleum-based diesel stream, with 60% diesel-range products and 20% each of gasoline and heavy-range products. Consistent with the above discussion, it has to be noted that compared to a petroleum-based Vacuum Gas Oil (VGO), biocrude heaviest components detected by chromatography are significantly lighter than the heavy end tail detected in VGO (Figure S1). An NMR analysis of the sample was also performed, in the case that some components did not elute in the GC analysis. As can be observed in Figure S2, besides strong signals in the 1-3 ppm region (saturates, olefins) and the 7-8 ppm region (aromatics), a signal is also observed in the 3.5-4.5 ppm region where phenols and methoxy groups generally appears. It can clearly be seen that this signal disappeared upon hydrogenation (Figure S2b). Meanwhile, the ratio of aromatic to saturate decreased, which is expected during hydroprocessing as detailed below.

This biocrude was subsequently hydrotreated in a fixed bed with commercial NiMo/alumina or NiW/silica-alumina catalyst, the characteristics of which are listed in Table S1. This type of catalyst is typically used for hydro-desulfuration and/or hydrocracking of middle distillate and VGO feeds in petroleum industry. It should be noted that more specialized catalysts have been developed for biomass containing feeds, in particular fats hydrogenation to diesel,[13-15] but were not used here to illustrate the ease of treatment of the biocrude. The catalyst was diluted with Silicon Carbide and presulfided before testing. Operating conditions ranged from 350 to 380ºC and 40 to 120 bars total pressure.

Table 1. Operating conditions, yields and product composition for the hydrogenation of biocrude, compared to some petroleum-based middle distillates. Operation temperature 350ºC and Weight Hourly Space Velocity = 1 h^{-1} unless specified. Yields and composition are given at 50h on stream.

Run	Feed	P	Cat.	Yields, wt%				Oil properties				Oil composition wt% [a]			
		bar				total	total	Boiling point (ºC)			density	Sat.	Mono	PNA	Oxyge-
				CO_2	CH_4	gases	oil	<216	216-359	>359	@ 20ºC		Arom.		nates
1	SRGO[b]	70	NiMo	-	<0.1	0.3	100	12.2	79.0	8.7	0.817	87.7	11.5	0.7	0.1
2	SRGO-LCO[c]	70	NiMo	-	<0.1	0.2	100	17.0	76.0	7.0	0.836	78.9	20.3	0.8	0.1
3	SRGO-BIO[d]	70	NiMo	-	0.2	0.7	97	17.9	74.9	7.9	0.831	83.0	16.5	0.5	0.1
4[e]	BIO	40	NiMo	0.1	0.7	1.9	87	33.3	57.4	9.3	0.916	40.1	44.6	10.7	4.6
5	BIO	70	NiMo	0.1	0.8	2.1	87	32.4	57.6	10.0	0.901	42.0	48.8	5.7	3.5
6	BIO	120	NiMo	0.1	0.7	1.9	88	38.1	56.3	5.5	0.891	56.6	41.9	1.2	0.3
7	BIO	120	NiW	0.2	0.6	1.6	87	37.5	56.7	5.9	0.892	56.3	42.1	1.1	0.6
8[g]	BIO	120	NiW	0.2	0.7	2.6	85	45.7	51.5	2.8	0.878	55.6	42.7	1.4	0.2

[a] Sat.: Paraffins and Naphthenes; MonoAr: mono-aromatics, including hydro-aromatics with tetralin or indane cores; PNA: Poly-Nuclear Aromatics [b] Straight Run Gas Oil. [c] Mixture with 20% Light Cycle Oil. [d] Mixture with 20% Biocrude. [e] WHSV = 0.5h^{-1} [f] Includes 1 to 2 wt% oxygenates compounds. [g] Temperature raised to 380ºC.

The lower bound of pressure ranges corresponds to the processing of easy-to-treat vegetable oils and other plant oils.[16,17] Meanwhile, the upper range is more characteristic of hydrocracking of heavier oil fractions. Such pressure has also been used in the processing of hydrothermal oils from lignocellulose or algae.[18,19] Space velocity was maintained at 1 h^{-1} for the different runs, but for processing pure Biocrude distillate at 40 bars, where space velocity was lowered at 0.5 h^{-1}.

A sample of Straight Run Gas Oil (SRGO) was also treated for reference purposes and presented a stable yield behavior after 50h on stream (Table 1). Very little gas was produced and the liquid product contained essentially paraffins and naphthenes, with some monoaromatics (less than 2%) and traces of poly-nuclear aromatics (PNA).

The reference stock was then mixed with 20% of either an aromatic oil stream commonly co-treated with SRGO in refinery (Light Cycle Oil, LCO, from Fluid catalytic Cracking), or 20% of the biocrude oil. LCO addition resulted in an increase in oil product density straightforwardly related to an increase in aromatics concentration.

The rather mild operating conditions (70 bars) did not allow to fully hydrogenate the aromatics in the LCO, but were sufficient to largely reduce poly-aromatics, maintaining its levels well below road diesel specifications (11 wt% maximum in EN590).

The processing of a similar amount of Biocrude (Run 3) gave better results, with a lower product density and a composition closer to that of the reference stock. The amount of CO_2 produced was negligible, and the amount of water (2 wt%) was in accordance with the oxygen content in the feed.

Thus, we have demonstrated that amounts of at least 20 wt% of biocrude can be co-treated with standard diesel, and that gives better results than co-treating 20% LCO as it is commonly done in the refinery.

To explore the limits of Biocrude processability, this stream was also treated as a pure feed under a variety of conditions. Pressure was varied from 40 to 120 bars with a NiMo catalyst (Run 4-6) resulting in high deoxygenation rate whatever the operating pressure. While some oxygenated compounds were detected when operating at 40 to 70 bars (3-5 wt%), only trace amounts (below 1 wt%) could be detected by GCxGC at a pressure of 120 bars. Oxygenated compounds of the phenols and benzofurans families may carry between 10 and 30 wt% oxygen, so that we can state that the hydroprocessed oil had an oxygen content around 1 wt% at 40-70 bars and below 0.3 wt% at higher pressures. This was confirmed by Elemental analysis of oxygen in the hydroprocessed oil as shown in Table S3. Again, water yield (10-12 wt% for Runs 4 to 8) was closely matched with the oxygen content of the biocrude feed, confirming near complete deoxygenation.

Gas was produced in yields of 2 to 3 wt%, with a minor contribution of CO_2 and a significant contribution of methane. Trading space velocity for pressure between 40 and 70 bars, an oil product with similar boiling range was obtained (Runs 4 and 5). Notwithstanding, increasing the operating pressure minimized the aromatic content, yielding a product with lower density.

A NiW catalyst was also used at 120 bars and 350ºC (Run 7) and gave similar results than NiMo (Run 6). Raising further reactor temperature and pressure to reach mild hydrocracking conditions (Run 8) decreased product density by reducing heavy ends and increasing the amount of light, gasoline-range products. Meanwhile, the hydroprocessed oil composition barely changed. For all the runs performed at 120 bars and 1 h^{-1}, poly-aromatics and oxygenated compounds were reduced to minimal amounts (below 2 wt% and 0.5 wt% respectively). While the density of the product remained slightly outside road diesel specifications (0.82 – 0.845), we believe this would be an excellent feedstock for diesel blending especially for the very paraffinic feedstocks obtained from the hydroprocessing of triglycerides (vegetable oils and others), which tends to have a low density.[17]

Baker and col. reported the severe hydroprocessing of a biocrude, yielding a fully deoxygenated product with a large gasoline fraction under the appropriate conditions.[20-21] The biocrude used in the present study had a higher H/C ratio, lower density and Conradson Carbon, hence improved processability so that a diesel range product with low oxygen content could be obtained under less severe hydrotreating conditions. A side effect of the lower process severity is the incomplete aromatic saturation, leading to a diesel with a high density as explained below.

A closer look at the GCxGC-MS analysis revealed that the oil product obtained from the biocrude contained a significant amount of polycyclic saturated products of the decaline families, as seen in Figure S3. The hydrogenated skeleton of terpene products of the family of resin acids, typically found in pine woods and the main constituents of pine resins were also observed. Furthermore, in the mono-aromatics region, a predominance of hydro-aromatic structures of the tetrahydronaphthalene, and decahydrophenanthrene families were found. Tetrahydrophenanthrene structures were classified into the Poly Nuclear Aromatics (PNA) group. All these compounds have a rather high density compared to paraffins and thus explain the high product density of the oil in spite of low levels of polyaromatics, and a significantly higher content of low molecular weight compounds in the streams produced from the 100% biocrude hydrogenation.

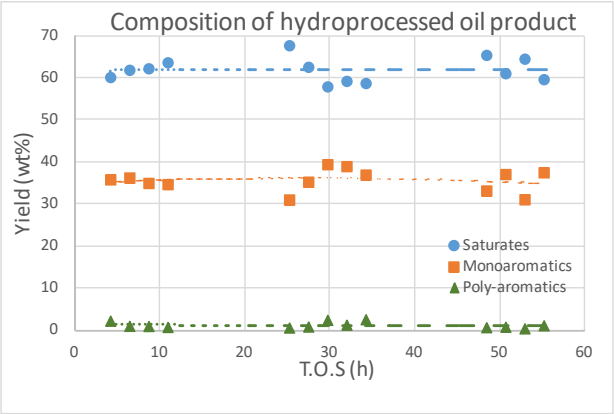

Figure 1. Composition of hydroprocessed oil product for Run 8 over the 56h Time-on-stream.

Catalysts after the hydrotreating runs were recovered, washed and analyzed by Elemental Analysis to check for the amount of coke formed (Table S2). Operating with biocrude at

pressure of 70 bars or lower substantially increased the coke on catalyst, which may cause accelerated deactivation. Note that under the most severe hydroprocessing conditions (Run 8), the coke on catalyst was only slightly higher than operating with SRGO. Indeed, under these conditions very stable yields and product compositions were obtained over the nearly 60 h of operation as shown in Figure 1.

Although we did not observe catalyst deactivation over the run length (60h), for lower pressures optimized catalysts should be used to ensure long term operation. Sulphur leaching can also be deduced from the spent catalyst Elemental Analysis (Table S3), when using sulphur free feed. This problem can be largely mitigated adding a sulfur compound to the feed.[22] Another simple strategy would consist in adding a small amount of SRGO in the feed mixture to provide sulphur and avoid deactivation.

In conclusion, we have demonstrated that a high quality, deoxygenated stream of hydrocarbons can be obtained from lignocellulose in three steps. The biocrude generated after hydrothermal liquefaction of pine wood, followed by separation and distillation, was successfully deoxygenated under refinery hydrotreating conditions in both blends and pure form. The quality of the final syncrude stream can be modulated depending on its final destination: selling to refinery for further upgrading may require only soft hydrotreatment (40 bars), while obtaining a finished product of enough quality for direct blending as transportation fuel use may require more severe hydrotreatment (120 bars, higher temperature) or specialized catalysts.

Experimental Section

Hydrotreatment. The fixed bed system (Figure S4) comprised a feeding tank, a gas system serving H_2, H_2S/H_2 and N_2, an HPLC pump, a tubular reactor, a tank for liquid condensation, a pressure control through a Back Pressure Regulator and gas exhaust. The liquid feed tank was heated at 60ºC and stirred to maintain the Biocrude Distillate at low viscosity. 4 grams of catalyst were mixed with Carborundum (Silicon Carbide, CSi) to adjust the total bed volume to 8 ml. An additional 1 ml CSi was added on the top of the bed. The catalysts were crushed and sieved into 0.2 to 0.8 mm particles to avoid any diffusion limitation during the reaction. The catalyst was sulphided at 400ºC with a stream of 10% H_2S in H_2 at 120 ml/min for at least 12 hours.

After pretreatment, the reactor temperature was adjusted to the desired set point and the system pressurized with hydrogen. Once the system was stabilized, feed injection was started. The hydrogen feeding rate was in large excess in order to ensure that the hydrogen partial pressure remained high at every point in the reactor. Flow rate was adjusted to 100 Nml/min, which represents 13.3 wt% of the feed, to be compared to the usual consumption for HDS (below 1 wt%) or even HDO of Biocrude Distillate, estimated in the range of 3-6 wt %.

Mass balances were performed periodically. The liquid product accumulated in the recovery tank during the test period was recovered and weighed. An aqueous phase usually forms a well defined layer at the bottoms of the liquids, and was easily extracted by pipetting. Karl-Fisher titration confirmed this phase was essentially water. It was also checked that the water content of the oily phase was negligible. Water yield determination had an uncertainty evaluated at ± 1 wt% of the feed for a water yield between 10 and 12 wt% for samples produced from 100% Biocrude. Gas samples taken downstream from the BPR valve were regularly analyzed during test period and the mean composition determined. CO, CO_2 and C_1-C_6 gas concentrations were determined by GC equipped with TCD/FID detectors. Coke yield was determined after the run by elemental analysis, and was found low enough (below 0.3%) not to be taken into account in periodical mass balance.

GCxGC configuration. An Agilent 5890 Gas Chromatograph coupled with an Agilent 5877A MS detector was used for this analysis. The system configuration is known as reverse GCxGC as the first column (HP-INNOWAX, 30m x 0.25mm x 0.25 µm) is a polar one, while the second one (DB5, 5m x 0. 25mm x 0.25 µm) is apolar. Injector temperature was set at 200ºC. Samples of 1 µl were injected with a split ratio of 100. Hydrogen carrier flows were 0.3 ml/min in the first column and 24 ml/min in the second one. A flow modulator was used. The modulation period was 4.5 s. The oven temperature was maintained at 50ºC for 5 minutes, then ramped at 2ºC/min ramp up to 250ºC, followed by a plateau for 60 minutes. The second oven followed the first oven program with a 10ºC offset. FID temperature was at 300ºC, acquisition frequency 100Hz. MS acquisition frequency was set at 14 spectra/s in a mass range of 40–360 amu. A response factor of 1.3 (compared to hydrocarbons) was used for oxygenated components.

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