Co-processing biomass fast pyrolysis and catalytic fast pyrolysis oils with vacuum gas oil in refinery hydroprocessing

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Abstract:

Fast pyrolysis and catalytic fast pyrolysis (CFP) have been considered to be promising approaches for converting lignocellulosic biomass into liquid bio-oils followed by upgrading to produce fuel-range hydrocarbon products. Co-processing fast pyrolysis and CFP bio-oils with petroleum feedstocks leverages the existing petroleum refining infrastructure, which reduces Capex for the overall conversion technologies for biomass to fuel and enables fast adoption of the technologies and biofuels. Here, we reported the co-processing of different woody fast pyrolysis and CFP bio-oils with petroleum vacuum gas oil (VGO) at 5-25% bio-oil blending levels over a NiMo sulfide catalyst for hydrotreating / mild hydrocracking. The catalyst activities over ~300 hours time on stream, the product yield and properties, and the biogenic carbon content in products are provided. Co-processing of the raw fast pyrolysis bio-oil in our configuration was not successful because the instability of the bio-oil resulted in reactor plugging and bio-oil stabilization by hydrogenation enabled their stable co-processing with VGO, whereas the CFP bio-oil can be co-processed without pretreatment. Simultaneous hydrodesulfurization, hydrodeoxygenation, and hydrocracking reactions occurred during co-processing and no obvious decrease in hydrodesulfurization and hydrocracking conversion of VGO was observed, suggesting the minimal impact of co-processed bio-oils on the reaction of VGO and also the simultaneous conversion of bio-oil and VGO to produce fuel products with much-reduced S and O content. Biogenic carbon content in co-processed products calculated by yield mass balance, together with results from isotopic measurements, indicates biogenic carbon incorporation into liquid hydrocarbon products. Higher biogenic carbon incorporation into fuel products was observed when co-processing CFP bio-oils than the fast pyrolysis bio-oils and over 90% of carbon in CFP bio-oil was incorporated into liquid hydrocarbon products.

Keywords: Co-processing; refinery; hydroprocessing; biomass; fast pyrolysis; catalytic fast pyrolysis; bio-oil; biogenic carbon

Introduction

Integration of biomass-derived feedstocks in a traditional petroleum refinery has gained a growing interest because of the increasing demand for low-carbon transportation fuels for the decarbonization of transportation sectors.[1,2,3] Co-processing petroleum feedstocks with biomass-derived feedstocks in the current refinery leverage the well-established technologies and existing petroleum refining infrastructure, which significantly reduces capital investment for the conversion technologies for biomass to biofuel production. It will enable a fast introduction of biofuels to the market and quick adoption of biomass conversion technologies. Lipids are the major biogenic feedstocks that are currently co-processed in existing refineries. However, lipid feedstock will be finite in the short-to-midterm, considering its increased demand, limited availability, and sustainability concerns. Therefore, biogenic liquid intermediates generated from lignocellulosic biomass (such as forest residues, agricultural wastes, and algae) and wastes (such as sewage sludge and organic municipal solid waste) from thermochemical liquefaction technologies (such as fast pyrolysis and hydrothermal liquefaction, HTL) will have great potential to provide the volumes required for co-processing to produce renewable biofuels.

Fast pyrolysis (FP) is the simplest and most cost-effective approach to producing a liquid intermediate, called bio-oil, from lignocellulosic biomass. However, bio-oil requires significant upgrading, mostly by hydrotreating, to produce biofuels, and its hydrotreating is challenging considering its instability, high oxygen and water content, and corrosiveness.[4,5,6] Bio-oil quality improvement, primarily on its stability, has been a major focus for FP bio-oil upgrading in recent years. Hydrogenation and catalytic fast pyrolysis (CFP) are the two promising approaches. Hydrogenation of bio-oil stabilizes the bio-oil by hydrogenating the reactive species, primarily carbonyl-containing species, and therefore enables improved stability.[5,6] CFP uses catalysts during fast pyrolysis, by *in situ* or *ex situ* configuration, toreduce oxygen content and associated reactive functional groups in the pyrolysis vapor and produce a water lean CFP bio-oil, which shows much-improved stability and enables direct hydrotreating without stabilization.[7-8] The final hydrotreating of these bio-oils is required to remove oxygen to produce hydrocarbon fuels and is mostly done by hydrotreating using catalysts similar to petroleum hydrotreating catalysts.[6, 8]

The report on co-processing of FP and CFP bio-oils is rather limited and, however, is increasing in recent years with a primary focus on upgraded/fractionated bio-oils. An early study by Pinheiro et al. [9] [10] used both model compounds and a membrane fractionated bio-oil combined with gas oil to explore the impact of co-processing bio-oil under industrial conditions and suspected that CO_x formation inhibits hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions. Alvarez-Majmutov et al. [11] reported the co-processing of deoxygenated pyrolysis bio-oil (1.4 wt.% O), a hydrotreating product from a FP bio-oil in light cycle oil (LCO), with vacuum gas oil (VGO) in a hydroprocessing pilot plant. They showed that co-processing of the deoxygenated pyrolysis bio-oil did not impact much catalyst stability and hydrocracking product yield but led to an increased hydrogen consumption. Dimitriadis et al [12] investigated the co-processing of a hydrotreated FP bio-oil (2.1 wt.% O) with a LCO at 10-30% volume blending ratio and showed negligible coke formation or process efficiency losses, reduced hydrogen consumption, and inhibition in the HDS activity. Bouzouita et al. [13] studied the co-processing in hydrocracking of a VGO with stabilized FP bio-oil (by partial hydrotreating, 37 wt.% O) and stabilized deoxygenated FP bio-oil (by deeper hydrotreating, 2.3 wt.% O) in a semi-batch stirred-tank reactor and suggested a decoupled hydrodeoxygenation (HDO) and hydrocracking process during the co-processing. Bergvall et al. [14-15] conducted co-processing of a raw FP bio-oil (43 wt.% O) with VGO in a continuous slurry hydrocracking process with an unsupported catalyst and reported a yield of biogenic carbon to gas (40-43 wt.%) and oil fraction (53-56 wt.%) and low coke yield. Their results suggest that slurry hydrotreating appears to be a promising technology for co-processing untreated FP bio-oils. Bio-crude derived from HTL of lignocellulosic biomass has also been studied for co-processing in hydrotreating.[16-18] More studies report the co-processing of vegetable oils, animal fats, and waste cooking oils with refinery streams in hydrotreating and hydrocracking.[19,20,21,22,23]

Here, we report the co-processing of different woody CFP and stabilized FP bio-oils with petroleum vacuum gas oil (VGO) at 5-25% bio-oil blending levels over a NiMo sulfide catalyst in a continuous flow fixed bed reactor under industrially relevant conditions for hydrotreating / mild hydrocracking. Four bio-oils, including two CFP bio-oils and two stabilized FP bio-oil, were used as biogenic feedstocks. We examed the catalyst activities over ~300 hours time on stream and determined the product yield and properties, and the biogenic carbon content in products. Our results showed that the CFP bio-oils and the stabilized FP bio-oils can be co-processed with VGO without detectable pressure drop increase in the reactor. Simultaneous HDS, HDO, and hydrocracking reactions occurred during co-processing and no obvious decrease in HDS and hydrocracking conversion was observed, suggesting the minimal impact of co-processed bio-oils on the reaction of VGO and also the simultaneous conversion of bio-oil and VGO to produce fuel products with much-reduced S and O content. Biogenic carbon content in co-processed products calculated by yield mass balance, together with results measured by isotopic methods, was used to indicate the biogenic carbon incorporation into fuel products.

Experimental methods

Feedstock and catalyst

Catalytic fast pyrolysis (CFP) bio-oils from forest residue and pine feedstock, denoted as CFP-A and CFP-B, respectively, were provided by NREL. A zeolite catalyst and *ex situ* CFP configuration was used over a two-inch fluidized-bed reactor. [24] The FP bio-oils from pine and forest residue were also provided by NREL. [25] The FP bio-oils were stabilized by hydrogenation at PNNL. [5,6] Specifically, the FP bio-oils were individually treated over a Ru/TiO_2 catalyst at 140 ^oC, 12.4 MPa, and 0.23 h^{-1} LHSV over 150 hours time on stream. The stabilized bio-oils were then collected, denoted as FP-S-A for stabilized FP bio-oil from pine and FP-S-B for stabilized FP bio-oil from forest residue, and used for co-processing study. A low metal, medium sulfur content vacuum gas oil (VGO) was used. Properties of the bio-oils and VGO will be provided in the result section. A commercial sulfided $NiMo/\gamma\text{-}Al_2O_3$ catalyst was used for this study and its property has been reported in detail in our previous publication.[26]

Co-processing tests

A bench-scale hydrotreater was used for the co-processing tests. The hydrotreater was configured as a single-pass, continuous, down-flow, and fixed catalyst bed reactor (Figure 1). It is described in detail in our previous publications.[27] The reactor was 63.5-cm-long Hastelloy C tubing with a 1.3 cm internal diameter. Mass flow controllers were used to feed H_2 and two ISCO pumps were used to feed bio-oils and VGO separately. After exiting the catalytic reactor, the liquid products were separated from the gaseous products in pressurized and cooled traps. The recovered liquid products were collected, phase-separated, weighed, and sampled for further analysis. The off-gas passed through the back-pressure regulator and was then directed through a DryCal gas meter to measure the gas flow rate and analyzed by an online Inficon Micro-GC 3000 four-channel micro-GC. The liquid products and outlet gas analysis data were collected over the entire period with individual products and data sets collected in an operating window of 12 hours. The hydrogen consumption in g H_2/g dry feed was calculated based on the feed flow rate and the difference of hydrogen inlet and outlet flow rate. The hydrogen outlet flow rate was calculated by the total outlet flow rate, based on the measured outlet flow rate by a volumetric flow meter with deduction of flowrate increase caused by the accumulation of liquid in the reactor system, and the hydrogen concentration measured by the micro-GC. The yields of organic, water, and gas products were determined based on the weight of the organic and water product and the outlet gas flow rate and composition.

For each test, 2 g catalyst (~3.5 ml) diluted by SiC (30-60 mesh) to a total of 10 ml was used. The diluted catalyst was placed in the isothermal zone of the reactor. A NiMo sulfide guard bed catalyst (~3 ml) was placed in the transition zone, between the entrance of the reactor and the catalyst bed to prevent any potential formation of high molecular weight species at the transition zone by providing catalytic activity. However, the transition zone was at a temperature range of 200-350 ^{o}C and therefore is expected to have a smaller contribution to the overall hydrocracking conversion compared to the main catalyst bed at 400 ^{o}C. The catalyst was pre-sulfided and, prior to the experiment, the catalyst was re-sulfided in the reactor by using a sulfiding agent (35% ditert-butyl-disulfide (DTBDS) in decane) and H_2 at 400 ^{o}C.

Each run was starting with VGO only and the bio-oil was then fed to the reactor by using a secondary pump for co-processing study. The bio-oils are not fully miscible with VGO and therefore the two feeds were introduced into the reaction by using the two separate pumps. The two feedstocks were then mixed in the transition zone of the reactor before reaching the main catalyst bed. The VGO was first fed into the system to break in the catalyst. As soon as a steady state was reached and sufficient data and product were collected, the bio-oil was then fed into the reactor when all other parameters, including VGO and H_2 flowrate, were kept consistent. The blending level was then varied, and steady-state samples were collected after at least 50 hours time on stream at the condition.

For all experiments, the reaction was conducted at 400 °C and 8.3 MPa total pressure. The liquid hourly space velocity (LHSV) of VGO was kept consistent at 2.0 h^{-1} during the test and H_2 to VGO ratio was kept consistent at 2000 L H_2/L VGO. Therefore, with co-feeding bio-oils, the actual LHSV of overall feed (VGO with bio-oil) was higher than 2.0 h^{-1} (see Table S1 in the supporting information).

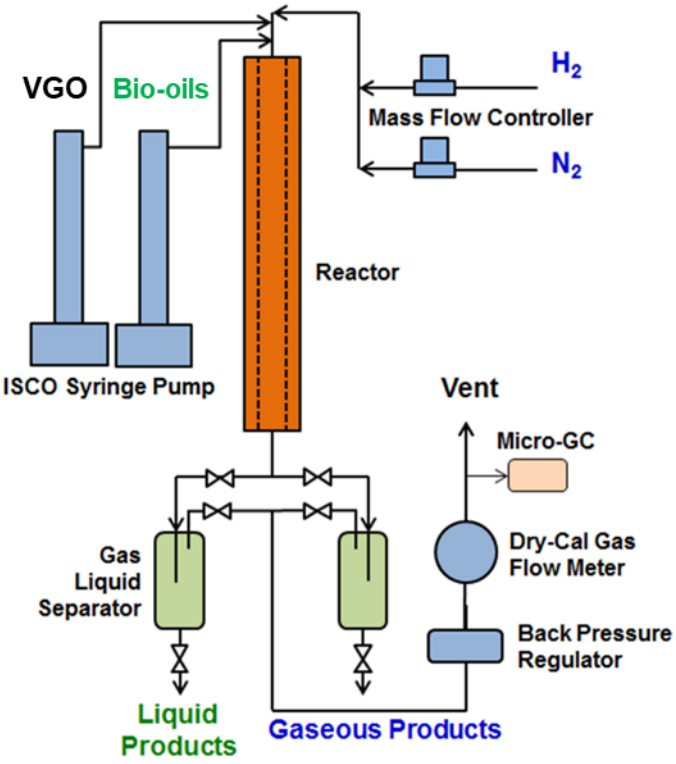

Figure 1. Schematic diagram of the bench-scale hydrotreater used for co-processing experiment

Feed and product analysis

Bio-oils, VGO, and hydrotreating products were analyzed for elemental components including carbon, hydrogen, nitrogen (ASTM D5291/D5373), O (ASTM D5373mod), S (ASTM D1552/D4239), and water content (Karl Fischer titration, ASTM D6869). For VGO feed and hydrocarbon products, sulfur content was measured by ASTM method D5453 and nitrogen content was measured by ASTM method D5762. Density measurements were conducted on a Stabinger viscometer (Anton Paar SVM 3000) at 20 ºC. The boiling point distribution of the VGO feed and co-processing products were determined by ASTM D7213, using a simulated distillation method that analyzes petroleum samples with extended boiling points beyond a typical #2 diesel. SARA (saturates, aromatics, resins, asphaltenes) heavy oil analysis was conducted with method IP-469.

Results and Discussion

Co-processing of catalytic fast pyrolysis bio-oil with VGO in hydrotreating / mild hydrocracking

The bulk properties of the five feedstocks, including VGO, two CFP bio-oils, and two stabilized FP bio-oils, used for this study were listed in Table 1. More analysis results of VGO, including simulated distillation and SARA analysis, will be provided in the later sections together with the hydrotreated products. The VGO feed has a sulfur content of 1.44 wt.% and a >350 ºC fraction of 96 wt.% by simulated distillation.

Table 1. Properties of the VGO, fast pyrolysis, and catalytic fast pyrolysis feed used in this study

	VGO	CFP-A	CFP-B	FP-S-A	FP-S-B
Density, g/ml at 20 ºC	0.925	1.129	1.138	1.086	1.123
Water content, wt.%	<0.01	6.4	5.7	31.3	19.9
Carbon, wt.%, dry basis	85.8	79.8	77.7	57.9	68.9
Hydrogen, wt.%, dry basis	11.8	6.8	6.8	7.6	7.5
H/C ratio, dry	1.64	1.01	1.04	1.55	1.30
Oxygen, wt.%, dry basis	0.85	12.6	14.5	34.5	23.5
Nitrogen, wt.%, dry basis	0.14	<0.2 [1]	<0.2 [1]	<0.2 [1]	<0.2 [1]
Sulfur, wt.%, dry basis	1.44	<0.03 [1]	<0.03 [1]	<0.03 [1]	<0.03 [1]

[1] Measured by elemental analysis.

Two CFP bio-oils were produced from forest residue (CFP-A) and pine (CFP-B) by using a zeolite catalyst. The CFP bio-oils contain substantial amounts of O (12-15 wt.%, dry basis) and water (5.7-6.4 wt.%). They are low in sulfur and nitrogen content. Their H/C ratio is around 1.0, suggesting the rich of aromatics in the bio-oils. It is consistent with the similar bio-oils produced by CFP using zeolite catalyst reported recently.[28,29] Upgrading of these CFP bio-oils in current reported research is conducted by hydrotreating using a single-bed conventional Ni or Co-promoted Mo-based sulfide catalyst at a relatively low LHSV of ~0.2 h^{-1} and a temperature of ~400 °C.[8,30,31] For a CFP bio-oil with similar O content, the yield of organic product based on dry CFP bio-oil is expected to be at around 60 to 80 wt.% and the produced oil contains 70 to 90 wt.% of hydrocarbon in the fuel range (gasoline and diesel, boiling point <350 ºC), depending on process configuration, the catalyst used, and biomass feedstock used. [8,30,31]

The hydroprocessing test started with VGO only. Product yield was calculated and gas and liquid samples were collected for analysis after reaching a steady state. The results are shown in Figures 2 and 3 and summarized in Table 1. H_2 consumption is 1.5 g H_2 per 100 g VGO. The density of the VGO-only product is 0.869 g/ml, lower than the feed of 0.925 g/ml. Simulated distillation results showed a <350 °C cut of 25.3 wt.% of the product, compared to 4.0 wt.% in the feed, which is equivalent to a 22% hydrocracking conversion. A small amount of <C_5 gas product was observed at a yield of 0.9 wt.%. HDS reaction occurred, with a decrease in sulfur content from 1.44 wt.% in feed to 0.089 wt.% in products, which is equivalent to a 94% HDS conversion. We did not use a reaction condition to reach a higher HDS conversion (>99%) to enable a rigorous comparison of HDS conversion after co-processing. Hydrogenation reaction also occurred, consistent with the increased H/C ratio (from 1.64 in feed to 1.82 in products) and reduced aromatic content analyzed by SARA analysis (from 63.8 in feed to 43.1 in products), as listed in Table 1. The results indicate hydrotreating and mild hydrocracking reactions were undergone for VGO with the catalyst and reaction conditions used.

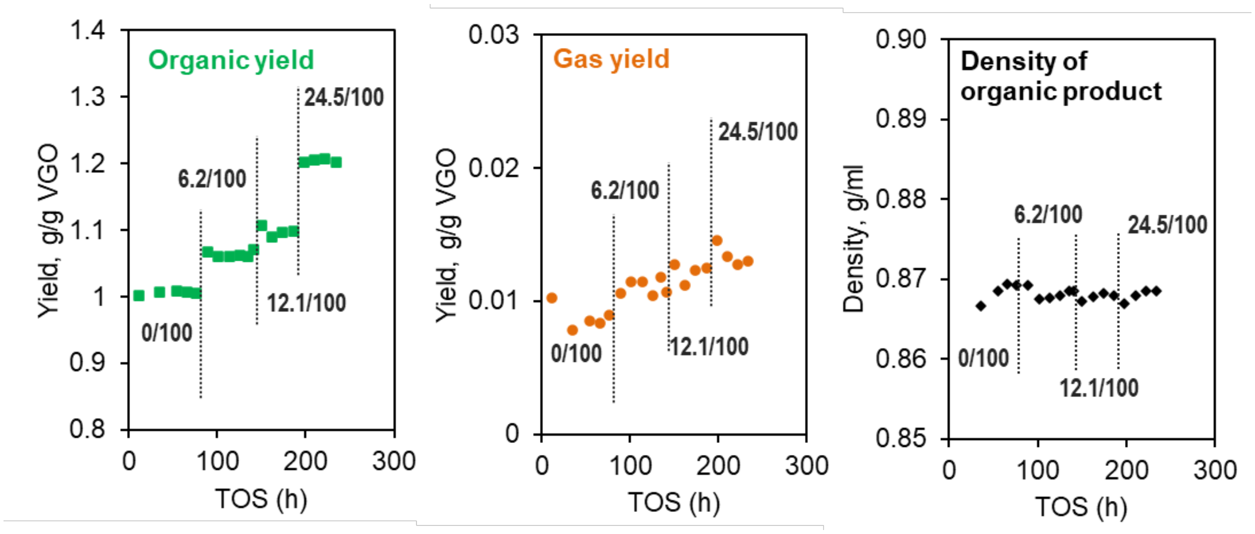

Figure 2. The yield of organic and gas products (based on VGO) and density of organic products at different times on stream with varied CFP-A bio-oil to VGO ratios.

Co-processing of the CFP-A bio-oil with the VGO was then conducted at three blending levels in bio-oil to VGO mass ratio of 6.2/100, 12.1/100, and 24.5/100. The liquid hourly space velocity (LHSV) of VGO and H_2 to VGO ratio were kept consistent during the test. During the ~300 hours time on stream test, no pressure drop increase along the catalyst bed was observed. However, it is unclear if coke formation could be significant at a much longer time on stream. It should be noted that a NiMo sulfide guard bed catalyst was required in the transition zone, between the entrance of the reactor and the catalyst bed, to prevent the potential formation of high molecular weight molecular species which could cause catalyst fouling and reactor plugging. The yield shown in Figure 2 is based on VGO feed only to show additional organic and gas product formation as a result of CFP bio-oil co-processing. Figure 3 shows the mass distribution of products as well as the mass input of feeds (VGO, bio-oil, and H_2). Note that for these calculations the mass balances have been normalized to 100%, whereas the actual mass balance is ranging from 96-102%. With co-processing of the CFP-A bio-oil, a higher H_2 consumption, a higher yield of organic products, and formation of water products were observed, suggesting the conversion of CFP bio-oils and incorporation of CFP-A bio-oil derived hydrocarbon in the co-processed products.

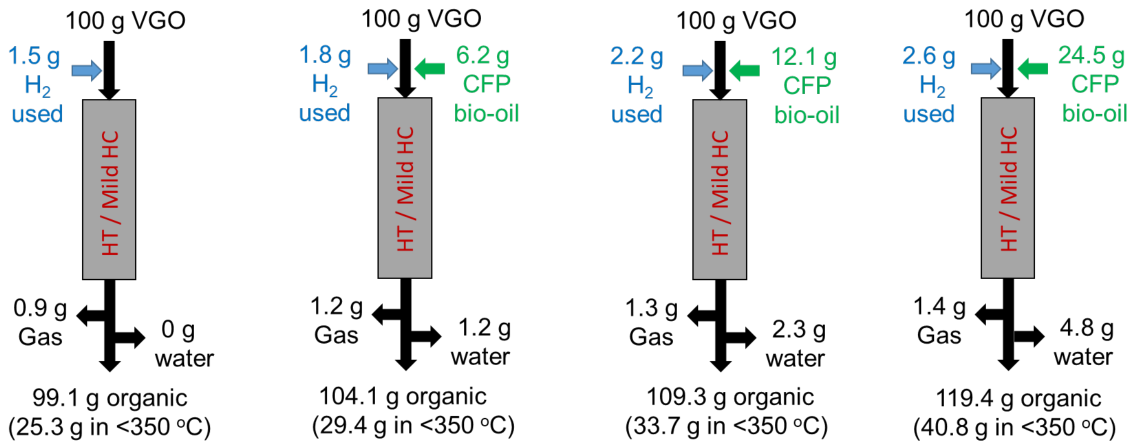

Figure 3. H_2 consumption and product distribution of co-processing the CFP-A bio-oil with VGO at 400 °C and VGO LHSV of 2.0 h^{-1}.

Co-processing the CFP-A bio-oil led to minimal change in the products. Figure 2 and Table 2 show almost no change in product density at different blending levels. A more detailed analysis of the products showed a similar carbon content, H/C ratio, and aromatic content. The sulfur content was even slightly lower in the co-processed products. Considering dilution of the organic product by bio-oil-derived products with almost no sulfur, we further calculated the sulfur conversion, which is 93.9% for VGO only, and 96.2%, 94.9%, and 95.2% for 6.2/100, 12.1/100, and 24.5/100 blending ratios for CFP-A, respectively. They are very similar and there is no trend of lower HDS conversion with higher bio-oil blending. Water content and O content were all below the detection limit, indicating the deep HDO of CFP bio-oil. The major difference between co-processed products compared with VGO-only product is their boiling point distribution. As shown in Figure 4, more light products at a boiling point below 350 °C were produced when co-processing the CFP bio-oils. Further calculated results shown in Figure 3 and listed in Table 1 indicate an increase in gasoline (<183 °C) and diesel (183-350 °C) range products. The < 350 °C fraction of products increased from 26.0% for VGO only to 34.2% for co-processing bio-oil at 24.5/100 bio-oil/VGO ratio. This agrees with the fact that woody CFP bio-oils normally produce hydrocarbon in the gasoline and diesel range after hydrotreating. For instance, our previous work showed that hydrotreating of a CFP bio-oil with an oxygen content of 16 wt.% led to organic products with a boiling point distribution of 46% for gasoline and 39% for diesel (determined by simulated distillation).[8] The gas products also changed slightly, including C1 to C5 alkanes (see Table S2 in the supporting information). However, a small content of CO_2 (4.4%) was detected at the highest CFP blending level.

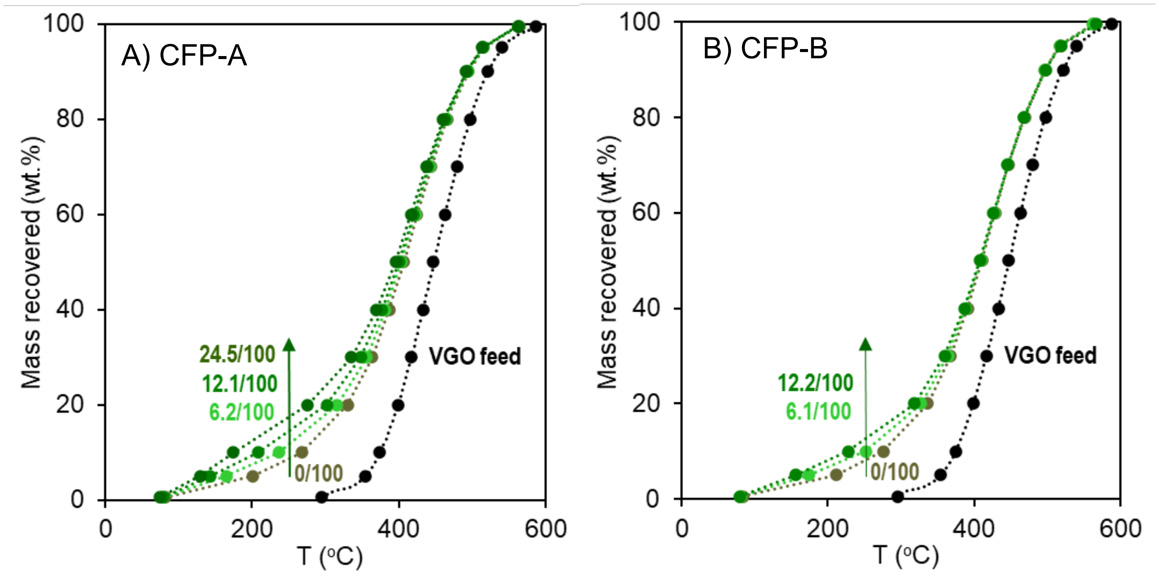

Figure 4. Boiling point distribution measured by simulated distillation for the VGO feed and products after VGO only hydroprocessing and co-processing VGO with CFP oils (A: CFP-A; B: CFP-B) at different blending levels.

Table 2. Properties of VGO feed and hydroprocessing products, including VGO only and CFP bio-oil co-processing with VGO.

		VGO feed	VGO-only	CFP-A/VGO			CFP-B/VGO	
				6.2/100	12.1/100	24.5/100	6.1/100	12.2/100
Density, g/ml at 40 °C		0.925	0.869	0.869	0.868	0.869	0.868	0.869
Water content, wt.%		<0.01	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Carbon, wt.%		85.8	86.2	86.5	87.1	87.7	86.1	85.7
Hydrogen, wt.%		11.8	13.1	13.2	13.3	13.3	12.6	12.9
H/C ratio, dry		1.64	1.82	1.83	1.83	1.82	1.77	1.81
Oxygen, wt.%		0.86	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Sulfur, wt.%		1.44	0.089	0.053	0.067	0.058	0.080	0.089
SARA Analysis	Saturates	33.6	56.9	-	56.9	-	-	54.1
	Aromatics	63.8	43.1	-	43.1	-	-	45.9
	Resins (Polars I)	2.1	<0.1	-	<0.1	-	-	<0.1
	Asphaltenes (Polars II)	0.5	<0.1	-	<0.1	-	-	<0.1
Sim-dist	<150 °C	0	2.3	4.0	5.5	7.2	3.9	4.7
	150-350 °C	4.0	23.0	24.2	25.3	27.0	23.1	23.7
	>350 °C	96.0	74.7	71.8	69.2	65.8	73.0	71.6

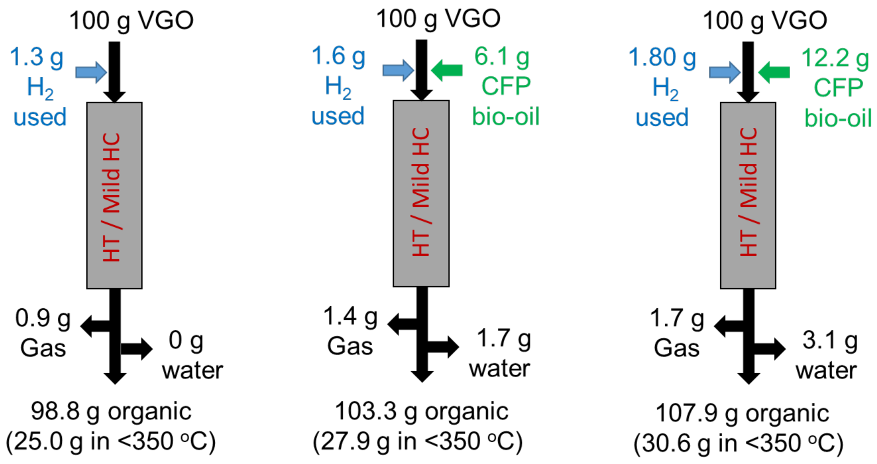

Figure 5. H_2 consumption and product distribution of co-processing the CFP-B bio-oil with VGO at 400 °C and VGO LHSV of 2.0 h^{-1}.

A similar test was conducted for co-processing the CFP-B bio-oil, generated from pine, and all results are shown in Figures 4 and 5 and Table 1. Only two blending level was used because of the limited availability of the bio-oil. As listed in Table 1, CFP-B bio-oil has a lightly high oxygen content (14.5 wt.%, dry basis) than CFP-A bio-oil (12.6 wt.%, dry basis). Similar performance as that for co-processing CFP-A bio-oil, generated from forest residue, was observed. The stable operation was achieved for over 200 hours time on stream. As shown in Figure 5, H_2 consumption and yields of organic products, water, and gas products are all increased when co-processing the CFP-B bio-oil. As to be elucidated in detail in the later section for yield calculation, the CFP-B bio-oil had a lower mass yield of the organic product than CFP-A, consistent with its higher O content. The product analysis summarized in Table 1 only shows some minor differences in the properties of the co-processed products from CFP-A and CFP-B bio-oils. Gas composition is provided in supporting information (Table S3). Co-processing of the CFP-B bio-oil resulted in a co-processed product with a lightly higher aromatic content and slightly fewer fuel products in the <350 °C range compared to CFP-A bio-oil. This probably is because of the intrinsic difference between the two bio-oils regarding their chemical composition, rather than their different influence on the VGO conversion when co-processing.

Our results indicate that the two CFP bio-oils from pine and forest residue, when co-processing with VGO at a blending ratio of < 25/100 (bio-oil/VGO, by mass), 400 ºC, and VGO LHSV of 2.0 h^{-1} and on a sulfided NiMo catalyst, have a minimal influence on reactions occurring with VGO, including HDS, hydrogenation, and mild hydrocracking. Simultaneous conversion of CFP bio-oil was observed with the formation of deoxygenated hydrocarbon largely in gasoline and diesel range, water, and light gas products. This occurs even when the overall LHSV was increased when co-processing bio-oils. As shown in Table S1, the overall LHSV is 2.20 and 2.40 at 12/100 and 24.5/100 blending ratios, respectively. Such increases in overall LHSV could also lead to a slower reaction of VGO, which however was not clearly observed. It suggested a decoupled bio-oil HDO and VGO hydrotreating/hydrocracking process during the co-processing, which agrees with the recent report by Bouzouita et al.[13] Under the reaction conditions we used, the HDO could be fast and the majority of the catalyst bed is treating a largely deoxygenated mixture. Therefore, the active site competition between oxygenates and other heteroatom species are minimal. This also agrees with Dimitriadis et al. [12] in that a higher reaction temperature can overcome the inhibition associated with hydrotreated FP bio-oil co-processing and Badoga et al. [18] that HDS is not significantly affected at co-processing ratios below 10 vol% and temperatures of 370 °C and above when co-processing a woody HTL bio-crude (oxygen content 10.6%). Water, introduced by and formed from bio-oil, does not impact the catalyst activity. However, it is unclear if it could impact catalyst stability by inducing a structural change of the catalyst at a much longer time on stream.[32] Pinheiro et al. [9,10] suspected that CO and CO_2 formation from bio-oils could inhibit HDS reaction. Here, CO_2, which was observed at the highest bio-oil blending level, is not believed to cause inhibition, probably because of the high reaction temperature and low CO_2 concentration.

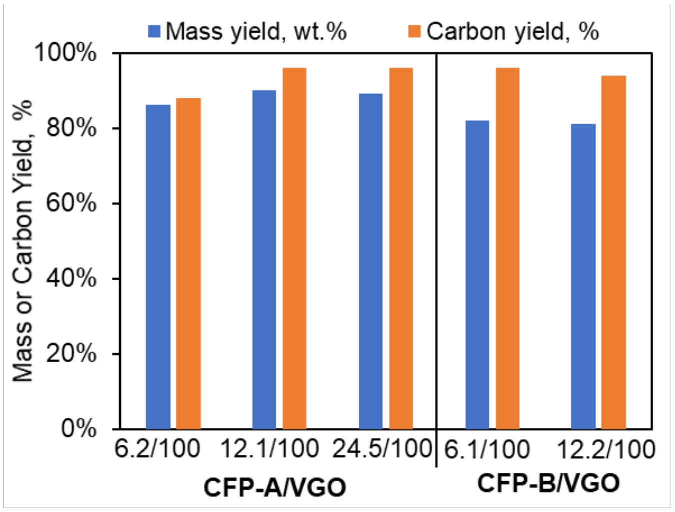

Figure 6. Mass, on a dry basis, and carbon yield of the biogenic organic product derived from CFP bio-oils when co-processing CFP bio-oils with VGO at different blending levels

We now calculate H_2 consumption and organic product yield originated from CFP bio-oil when co-processing by assuming that all additional H_2 consumption and yield of water, gas, and liquid products, compared to VGO only baseline, are from the CFP bio-oil and there is no change of VGO conversion, including H_2 consumption, gas yield, and boiling point distribution. The data shown in Figures 3 and 5 are used for the calculation. Figure 6 reports the calculated mass yield of the biogenic organic products derived from CFP bio-oil per dry CFP bio-oil. For CFP-A bio-oil, the mass yield on a dry basis is in the range of 86 to 90%, whereas for CFP-B bio-oil, it is in the range of 81-82%. The higher organic product yield from CFP-A than CFP-B bio-oil agrees with what the lower O content, on a dry basis, in CFP-A than CFP-B. As to the H_2 consumption, CFP-A co-processing is 0.05-0.06 g H_2 per g dry bio-oil and CFP-B co-processing is 0.04-0.05 g H_2 per dry bio-oil. Lower H_2 consumption of CFP-B bio-oil agrees with the slightly lower H/C ratio and higher aromatic content for co-processed products of CFP-B bio-oil compared to CFP-A bio-oil. We further calculated the content of <350 °C range product in bio-oil derived fuels, which is in the range of 76-82% for CFP-A bio-oil and 62-64% for CFP-B bio-oil. The overall H_2 consumption, organic product yield, and organic product properties associated with bio-oils during co-processing are similar to that observed for upgrading CFP bio-oils in stand-alone hydrotreating. For instance, our previous work showed that hydrotreating of a CFP bio-oil with an oxygen content of 16 wt.% led to an organic product yield of 76% and the content of <350 °C range product of 84%.[8] We do not report the oxygen/water balance here as the calculation showed a variation of oxygen/water balance in the range of 80-100% for the two CFP oils. It is largely because of the difficulties in accurately measuring the water yield at the scale of testing we used here.

With a similar method, we calculated the carbon mass balance and carbon yield based on mass yield and carbon content of feed and products. Note that for these calculations the carbon balances have also been normalized to 100%. The results are provided in Figure 6. For CFP-A bio-oil, the carbon yield of fuels derived from bio-oil is in the range of 88 to 96%, whereas for CFP-B bio-oil, it is in the range of 94-96%. It is also similar to the stand-alone hydrotreating results of a similar bio-oil. The result suggests that more than 90% of biogenic carbon was incorporated into the fuel products. The loss of biogenic carbon is by gas ($<C_5$) formation.

Based on carbon yield, we can then calculate the biogenic carbon content in fuel products and then compare it with the biogenic carbon content determined by the isotope methods including the ^{14}C Accelerator Mass Spectrometry (AMS) method and the $\delta^{13}C$ method. The products from the co-processing of CFP-A bio-oils have been analyzed by the ^{14}C AMS method and the $\delta^{13}C$ method. The results and the detailed methodology of the ^{14}C AMS method and the $\delta^{13}C$ method have been reported in our recent publication.[33] The results are replotted and shown in Figure 7.

In general, there is a good agreement between the three methods, further indicating the high incorporation of biogenic carbon in CFP bio-oils into co-processed organic hydrocarbon products. The biogenic carbon content estimated by the yield mass balance approach here is generally higher than those from the ^{14}C AMS method and the δ^{13}C method, especially for the samples with a high CFP blending ratio. It probably suggests that, at a high blending ratio, there is minor inhibition on hydrocracking of VGO by bio-oil, which leads to less gas formation from VGO. Therefore, the gas yield from CFP should be higher than that calculated here by assuming no change in VGO conversion. An analysis of biogenic carbon content in gas products will help to address this question, which will be conducted in our future research. Note that the accuracy and precision of biogenic carbon content calculated from the yield mass balance method should be much improved with testing at a larger scale. We are here using a bench-scale reactor with 2 g of catalyst, which could lead to substantial errors, such as the challenges in accurately measuring water yield mentioned above. However, developing methods for measuring biogenic carbon content in the co-processed product is not within the scope of this paper and there are several recent reports on biogenic carbon content determination for co-processed products. [34,35,36,33]

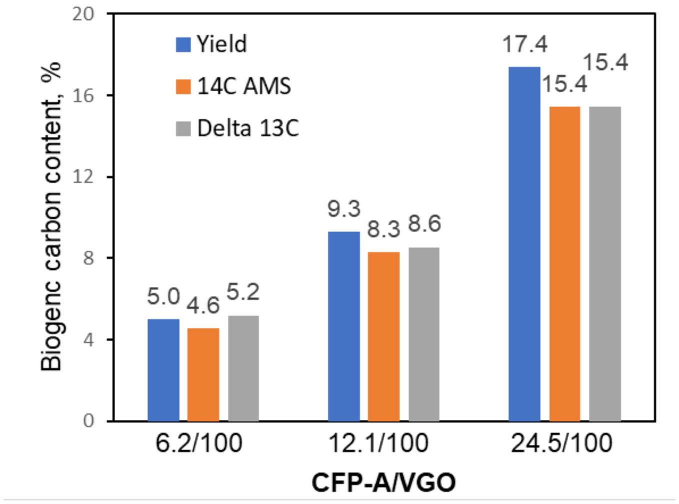

Figure 7. Comparison of biogenic carbon content in co-processing products obtained by yield mass balance method (blue), ^{14}C AMS method (orange), and $\delta^{13}C$ method (gray). (Reproduced from Figure 3 of ref [33], Copyright [2020] American Chemical Society.).

Co-processing of fast pyrolysis bio-oil with VGO in hydrotreating / mild hydrocracking

Co-processing of raw fast pyrolysis (FP) bio-oil was much more challenging compared to that of CFP bio-oil because of its instability, high water content, and inhomogeneity. We attempted direct co-processing raw FP bio-oil with VGO, which resulted in reactor plugging within 30 hours time on stream. It agrees with the fact that significant stabilization is required for FP bio-oil to be hydrotreated in the fixed bed hydrotreating reactors.[6,5, 37] One promising technology for FP bio-oil upgrading involves two-step processes: a low-temperature hydrogenation step using reduced metal catalyst followed by a high-temperature hydrotreating step using sulfide hydrotreating catalysts. Therefore, the FP bio-oils for this study were treated by hydrogenation to stabilize them.[5,6] Specifically, the pine bio-oil and the forest residue bio-oil were individually treated over a Ru/TiO_2 catalyst at 140 °C, 12.4 MPa, and 0.23 h^{-1} LHSV over 150 hours time on stream. A slow deactivation of the catalyst was observed because of sulfur poisoning and the carbonyl content of the products gradually increased with time on stream. [5,6]The products with a carbonyl content below 1.5 mmol/g were collected and mixed as feed for co-processing. Our previous research demonstrated that a pine or oak bio-oil with a carbonyl content below 1.5 mmol/g after hydrogenation stabilization can be processed in a hydrotreating reactor at 400 °C without causing catalyst bed fouling and plugging for at least 1000 hours on stream.[35] The stabilized bio-oils, however, showed phase segregation. In order to get a steady feeding of the stabilized bio-oil for co-processing tests, 10 wt.% of methanol was then added to the stabilized bio-oil. All the analysis, yield, and hydrogen consumption data below have excluded the methanol by assuming that methanol has been fully converted to methane ($CH_3OH + H_2 \rightarrow CH_4 + H_2O$) during co-processing.

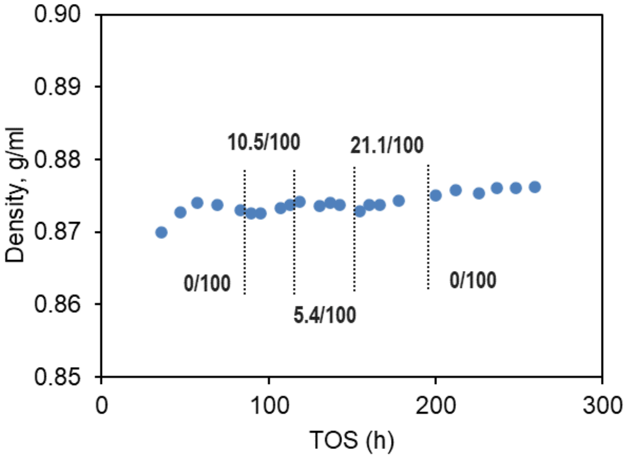

Figure 8. The density of organic products at a different time on stream with varied FP-S-A bio-oil to VGO ratios.

As shown in Table 1, the two stabilized FP bio-oils, FP-S-A from pine and FP-S-B from forest residue, showed a high water and oxygen content. They also had a relatively high H/C ratio because of the hydrogenation reaction during the stabilization process. The FP-S-B from forest residue had a lower oxygen and water content than FP-S-A from pine. Direct hydrotreating of the stabilized FP bio-oil can be conducted by using a single-bed conventional Ni or Co-promoted Mo-based sulfide catalyst at a relatively low LHSV of ~0.2 h^{-1} and a temperature of ~400 °C. The produced organic product from hydrotreating similar FP bio-oils, such as a typical pine bio-oil,[38] showed significant removal of O to < 1 wt%. The yield of produced fuel based on dry FP bio-oil was at around 40 to 50 % and the produced oil contains 70 to 90 % of hydrocarbon in the fuel range (gasoline or diesel, boiling point <350 ºC), depending on process configuration, the catalyst used, and biomass feedstock used. Gas and water were also formed in a relatively large yield.

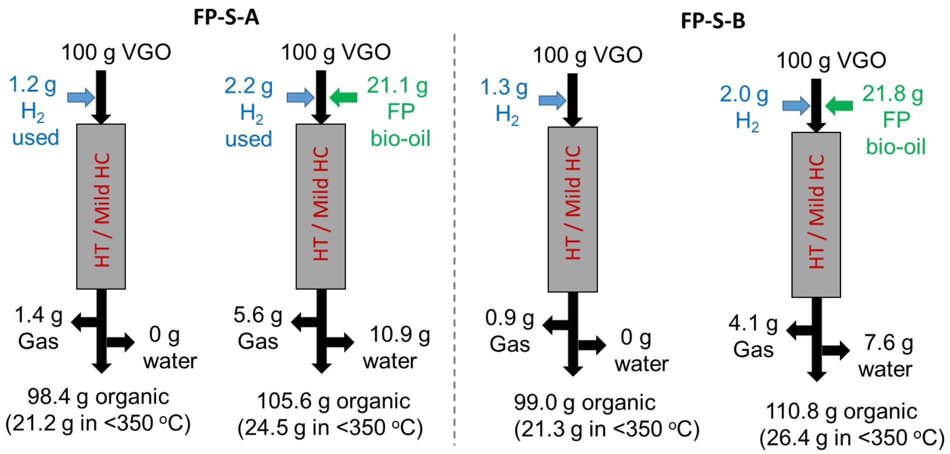

Figure 9. H_2 consumption and product distribution of co-processing the FP-S-A and FP-S-B stabilized FP bio-oil with VGO at 400 °C and VGO LHSV of 2.0 h^{-1}.

Table 3. Properties of VGO feed and hydrotreating / mild hydrocracking products, including VGO only and stabilized FP bio-oil co-processing with VGO.

		VGO feed	VGO-only	FP-S-A/VGO			FP-S-B/VGO	
				5.4/100	10.5/100	21.1/100	5.6/100	21.8/100
Density, g/ml at 40 °C		0.925	0.874	0.873	0.874	0.874	0.875	0.879
Water content, wt.%		<0.01	<0.1	<0.2	<0.2	<0.2	<0.2	<0.2
H/C ratio, dry		1.64	1.76	1.80	1.77	1.81	1.76	1.67
Oxygen, wt.%		0.86	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Sulfur, wt.%		1.44	0.090	0.12	0.13	0.070	0.074	0.12
Sim-dist	<350 °C	4.0	21.5	22.1	23.3	23.2	22.2	23.8
	>350 °C	96.0	78.5	77.9	76.7	76.8	77.8	76.2

The co-processing tests for the two stabilized FP bio-oils were conducted following a similar procedure and conditions to that for the CFP bio-oils. Three and two blending ratios, ranging from 5/100 to 22/100 bio-oil to VGO ratio, were used for FP-S-A and FP-S-B, respectively. During the ~300 hours time on stream test for each bio-oil, no pressure drop increase was observed. Similar to CFP bio-oil co-processing, it is unclear if coke formation could be significant at a much longer time on stream test and a NiMo sulfide guard bed catalyst was required in the transition zone. Figure 8 is the change of organic product density at a different time on steam during the test for FP-S-A. Figure 9 shows the mass distribution of products, as well as the mass input of feeds (VGO, bio-oil, and H_2) for the two ~20/100 blending ratios. More data for other blending ratios are included in the supporting information (Figures S1 and S2). The properties of the products are summarized in Table 3. In general, conversion of FP bio-oil occurred and led to the formation of water, increased yield of gas product, and increased hydrogen consumption. The water content and oxygen content in the co-processed organic products were below the detection limit, indicating deep deoxygenation from FP bio-oils during co-processing. Similar to that observed for CFP bio-oil co-processing, minimal impact of stabilized FP bio-oil to the conversion of VGO was observed. The density, H/C ratio, and sulfur content of the organic products, with and without co-processing, are largely unchanged. Simulated distillation results showed an increased content of light products at a boiling point below 350 ºC when co-processing bio-oils. For the test of FP-S-A, after finishing the co-processing test, we further evaluated performance with the VGO only at the same condition as that before co-processing to evaluate the impact of co-processing on the catalyst. Product analysis showed a minimal difference between the VGO-only products before and after co-processing. Specifically, density was 0.874 and 0.876 g/ml, sulfur content was 0.09 and 0.05 wt.%, H/C ratio was 1.76 and 1.75, and <350 ºC content was 21.5 and 20.8 wt.%, before and after co-processing of FP-S-A, respectively. These results further indicate that two stabilized FP bio-oils from pine and forest residue, when co-processing with VGO at the conditions used here, have a minimal influence on reactions occurring with VGO, including HDS, hydrogenation, and mild hydrocracking. Simultaneous conversion of bio-oil was observed with the formation of deoxygenated hydrocarbon largely in gasoline and diesel range, water, and light gas products. This, together with the results CFP bio-oil co-processing, suggests the decoupled bio-oil HDO and VGO hydrotreating/hydrocracking process during the co-processing of CFP and FP bio-oils from woody feedstock under the reaction conditions we used.

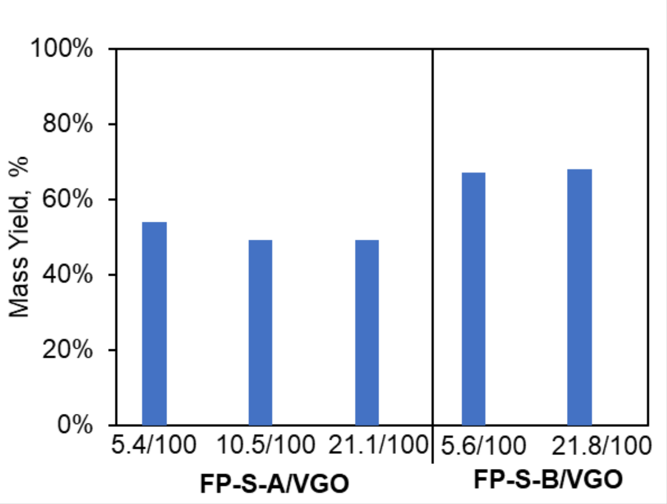

Figure 10. Mass yield of biogenic fuel derived from stabilized FP bio-oils, on a dry basis, when co-processing bio-oils with VGO at different blending levels.

The mass yield of the biogenic organic product derived from stabilized FP bio-oils when co-processing them with VGO at different blending levels was also calculated following a similar method described above. Figure 10 reports the calculated mass yield of the biogenic organic product derived from stabilized FP bio-oil per dry bio-oil. For FP-S-A bio-oil, the mass yield on a dry basis is in the range of 49 to 54%, whereas for FP-S-B bio-oil, it is in the range of 67-68%. The lower organic product yield from FP-S-A than FP-S-B bio-oil agrees with what the higher O content, on a dry basis, in FP-S-A (34.5 wt.% O) than CFP-B (23.5 wt.% O). The overall organic product yield is largely similar to that observed for upgrading FP bio-oils in stand-alone hydrotreating.[25] As expected, the mass yield of the biogenic organic product derived from stabilized FP bio-oils is much lower than that from CFP bio-oils.

Conclusion

In summary, different woody CFP and stabilized FP bio-oils were co-processing with petroleum vacuum gas oil (VGO) at 5-25% bio-oil blending levels for hydrotreating / mild hydrocracking. Co-processing the raw FP bio-oil at our conditions was not successful because the instability of FP bio-oil resulted in reactor plugging. Hydrogenation was able to stabilize the FP bio-oil and enable their co-processing. Both stabilized FP bio-oil and CFP bio-oil, without pretreatment, can be co-processed with VGO without detectable pressure drop increase in the reactor. Simultaneous HDS, HDO, and hydrocracking reactions occurred during co-processing and no obvious decrease in HDS and hydrocracking conversion of VGO was observed, suggesting the minimal impact of co-processed bio-oils on the reaction of VGO and also the simultaneous and decoupled conversion of bio-oil and VGO to produce fuel products with much-reduced S and O content. Biogenic carbon content in co-processed products was calculated by yield mass balance and compared with the results measured by isotopic methods. High biogenic carbon incorporation into fuel products was observed, especially for CFP bio-oils. Specifically, over 90% of carbon in CFP bio-oil used in this study was incorporated into liquid hydrocarbon products. Our further work will include larger-scale testing for more accurate yield calculation and production of sufficient oil product for fractionation to get fuel fraction for biogenic carbon distribution determination and longer-term testing and characterization of the used catalyst to understand the potential impact on the catalyst stability.

Supporting Information

The following files are available free of charge: Reaction conditions; Gas product composition; and H_2 consumption and product distribution of co-processing the FP-S-A and FP-S-B stabilized FP bio-oil.

Conflicts of Interest

There are no conflicts to declare.

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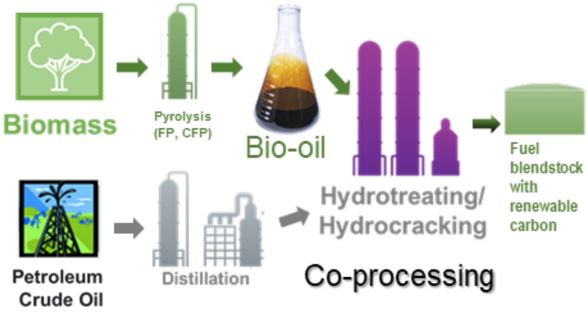
TOC Graphic


Biomass
Pyrolysis (FP, CFP)
Bio-oil
Hydrotreating/ Hydrocracking
Fuel blendstock with renewable carbon
Petroleum Crude Oil
Distillation
Co-processing