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Production of biofuels via co-processing in conventional refining processes

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ABSTRACT

Production of second-generation biofuels via gasification followed by Fischer–Tropsch synthesis is receiving increased attention due to the high-quality fuels produced. Although this process scheme produces fuel components compatible with conventional fossil fuels, the high-investment cost associated with its commercial application renders this option economically unfeasible. For this reason other process schemes are explored, primarily aiming to lower investment costs. Such options include co-processing liquids from biomass flash pyrolysis in refining processes like fluid catalytic cracking (FCC) or in hydroprocessing. Vegetable oils could also by hydroprocessing with petroleum oils. In this paper small-scale pilot plant results will be presented from the following three process schemes aiming to the production of high-quality biofuels: (i) catalytic pyrolysis of biomass over FCC zeolitic catalysts at moderate temperatures. From this process the effect of catalyst on the yields of coke, gaseous and liquid products will be reported. (ii) Co-processing gas oil mixed with hydrotreated biomass pyrolysis liquids. It will be shown that, depending on the concentration of biomass liquids, this option is technically viable for FCC units. (iii) Co-hydroprocessing vacuum gas oil (VGO) with sunflower oil to produce mid-distillates, mainly gasoline and diesel. For this option catalysts and process conditions will be discussed.

1. Introduction

Biomass is today the main renewable energy source available, producing via various biological and thermochemical conversion processes liquid, solid and gaseous fuels. Existing technologies for the conversion of biomass to first generation biofuels use only a small part of the biomass and offer questionable CO_2 benefits. Lignocellulocic biomass is used for the second generation biofuels, requiring however high-investment costs leading to expensive fuels [1–3]. Another option for affordable biofuels production is the use of various low-cost bio-based liquids into existing petroleum refining infrastructure, requiring little capital cost investment. In this paper, we discuss the feasibility of biofuels production by co-processing bio-oil or vegetable oils using the catalytic cracking and the hydrotreating refining technology [4,5]. The production of improved quality bio-oil by an in situ biomass catalytic pyrolysis step is also discussed.

The first bio-based liquid investigated in this paper as co-feedstock in conventional refineries is bio-oil or biomass flash pyrolysis liquids (BFPL), which is produced in high yields by the biomass fast pyrolysis process. Several review papers involving technologies and operating variables for optimizing bio-oil production and quality are available [2,3,6,7]. The main process variables that strongly affect the process are temperature, heating rate and fast quenching of vapors, in order to prevent secondary cracking of the bio-oil components to lighter products [3,5,8]. Based on these principles, several reactor configurations have been proposed in the literature, aiming mainly at the maximization of the liquid yields [3]. Among them are bubbling fluidized beds, circulating fluid beds (CFB), transported beds and rotating cone reactors [9–11]. Biomass conventional pyrolysis liquids have been used in boilers and furnaces and sometimes in diesel engines, for the production of heat or electricity [3,12]. Bio-oil is also a very important source of renewable chemicals, however, it cannot be used as a transportation fuel directly without a prior upgrading step. This is due to their high oxygen (40–50%) and water (15–30%) content, the limited stability and the high acidity [7,12].

The upgrading of the bio-oil into a transportation fuel of improved quality was studied either via in situ processes (within

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Abbreviations: BFPL, biomass fast pyrolysis liquid; CFB, circulating fluidized bed; DMDS, dimethyl-disulfide; FCC, fluid catalytic cracking; GHV, gross heating value; HBFPL, heavy fraction of biomass fast pyrolysis liquid; HCO, heavy cycle oil; HDN, hydrodenitrogenation; HDO, hydrodeoxygenation; HDS, hydrodesulfurization; HDT, hydrotreating; HPLT, high-pressure low temperature; LBFPL, light fraction of biomass fast pyrolysis liquid; LCO, light cycle oil; LHSV, liquid hourly space velocity; MAT, micro-activity test; MCRT, micro-carbon residue tester; TPA, tetra-propyl-amine; VGO, vacuum gas oil.

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the pyrolysis reactor) or via downstream processes. For the in situ upgrading of bio-oil a selective catalyst is used as a heat carrier, aiming at the catalytic upgrading of the biomass pyrolysis vapors (catalytic pyrolysis). From the limited literature in biomass catalytic pyrolysis, it seems that bio-oil of improved quality can be produced but with additional water and coke-solid residue formation, in expense of the organic phase of the bio-oil. However, the type of catalyst may play a significant role in the quality of the bio-oil [13–15]. Of course more research is needed in this issue.

Regarding the downstream upgrading processes of bio-oil, there are two main investigated routes: hydrodeoxygenation (HDO) and catalytic cracking (FCC) [4,16–24]. The current state of the art in HDO is based on the hydrotreatment of bio-oil over heterogeneous catalysts (CoMo- and NiMo-based catalysts) with high-pressure hydrogen at moderate temperatures (330–450 °C). The FCC pathway employs mainly zeolite Y and ZSM-5 catalysts in micro-activity test (MAT) type reactors. Both upgrading technologies exhibit major operating problems (e.g. reactor plugging, rapid catalyst de-activation) and low-liquid product yields [25], due to the bio-oil tendency to polymerize even under mild heating. In this work a process scheme for the co-processing of bio-oil into refinery is suggested along with experimental results.

Besides bio-oil, another feedstock that can be used as co-feed in conventional refining processes is vegetable oil. Vegetable oil is a renewable feedstock currently being used for biodiesel production through transesterification. The biodiesel production economics depend on selling glycerol byproduct, the price of which decrease with increasing biodiesel production [25]. The feasibility of biofuels production by hydrotreating vegetable oil is investigated in this paper. In order to use existing petroleum refinery processes to convert vegetable oil to diesel fuel, the vegetable oil need to be hydrotreated in analogy to the petroleum-derived feedstocks. Hydroprocessing is a well-known technology within the petrochemical industry, for upgrading heavy hydrocarbon molecules. However, hydroprocessing recently appears as an alternative technology for producing biofuels [26,27]. Hydrotreating has been previously used to produce straight chain alkanes ranging from n-C_{15} to n-C_{18}, include in the fatty acid fraction of tall oil and other vegetable oils. The normal alkanes produced have a high-cetane number with acceptable cold flow properties. Neste oil has already commercialized such technology producing diesel fuel from vegetable oil by a modified hydrotreating process [28]. Finally for co-hydroprocessing of vegetable oil, acidity and corrosion limitations should be considered for scaled up to industrial reactors [29].

In this work small-scale pilot plant results will be presented from the following process schemes: (i) biomass catalytic pyrolysis, where biomass is brought in contact with FCC zeolitic catalysts at moderate temperatures. (ii) Hydrotreating biomass pyrolysis liquids to reduce the oxygen content and then co-processing gas oil mixed with the hydrotreated pyrolysis liquids in an FCC unit. (iii) Co-hydroprocessing VGO with sunflower oil to produce fuels of similar properties with conventional fossil fuels. All these studies will show that co-processing of biobased liquids with petroleum fractions in existing refinery processes is feasible, however more research and technology improved are required.

2. Experimental units

2.1. The biomass catalytic pyrolysis unit

In Fig. 1 a detailed schematic view of the CPERI biomass catalytic pyrolysis small-scale pilot plant unit is presented. The experimental system is fully automated and consists of a biomass and a solid feed section, a reactor and a product recovery line. The biomass feed section includes a 4-l cylindrical hopper and a screw feeder, which control the biomass flow into the reactor. The solids feed system includes a 30-l fluid bed regenerator vessel. The purpose of the regenerator is to regenerate the spent catalyst and to supply the catalyst with the required heat for the biomass pyrolysis reactions. The regenerator is connected to the reactor through a heated transfer line with a slide valve controlling the catalyst flow to the reactor during the experiment. The reactor consists of an injector and a riser section. The injector is designed to promote the direct mixing of the hot catalyst with the biomass particles. The riser is a 5-m long vertical tube of 6.2 mm internal diameter. Gases and solids leaving the riser enter tangentially into the cyclonic head of the stripper that allows solids removal. The

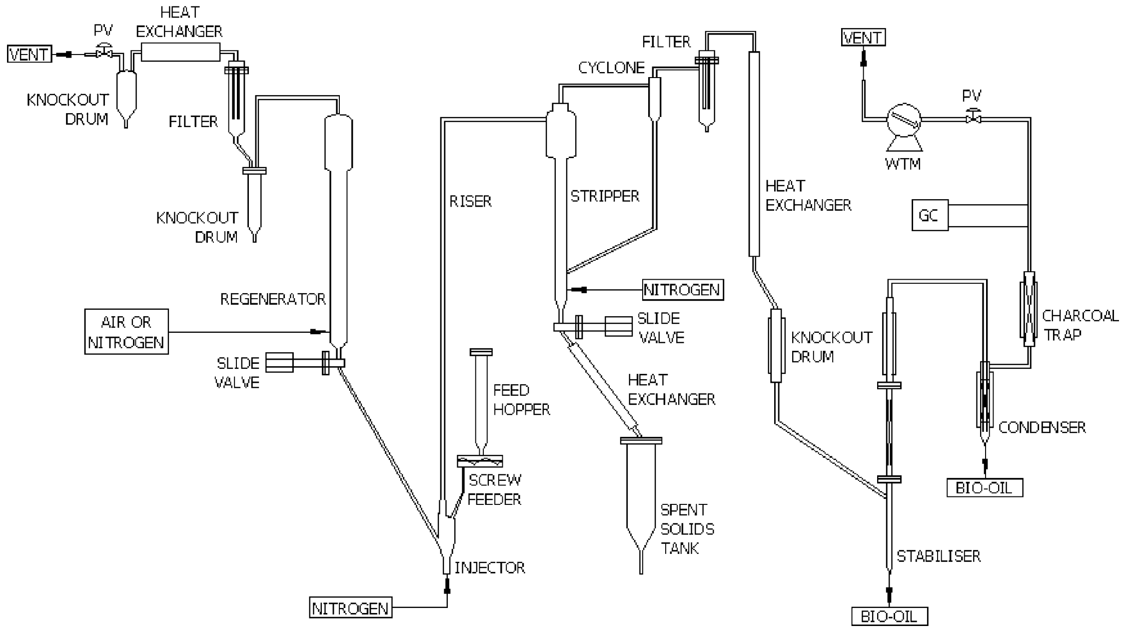

Fig. 1. Schematic diagram of the CPERI biomass pyrolysis small-scale pilot plant unit. The biomass is introduced from feed hopper through screw feeder. The solid material is coming from the regenerator through the slide valve.

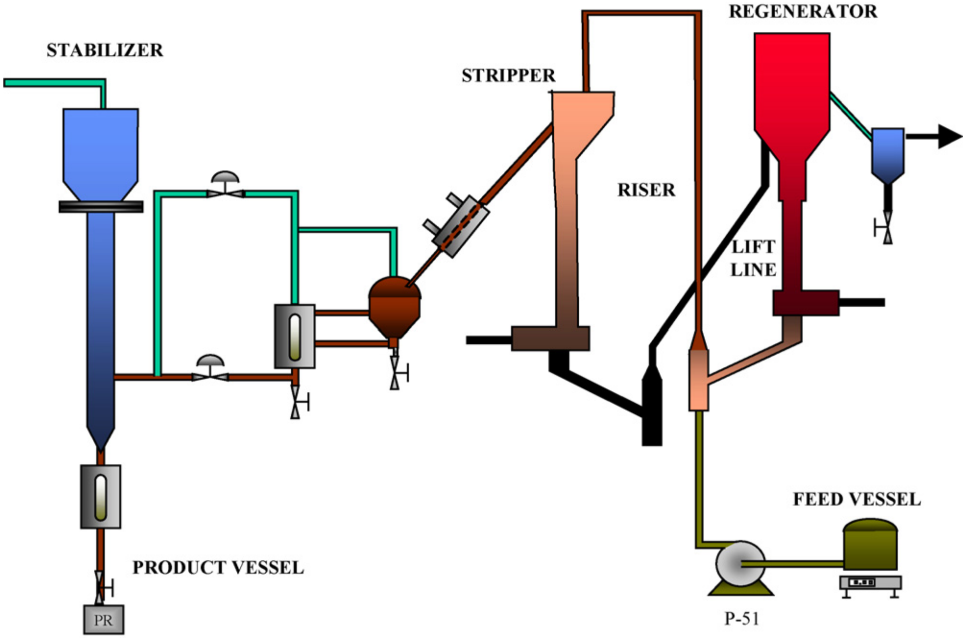

Fig. 2. Schematic diagram of the CPERI FCC small-scale pilot plant. The co-feed of hydrotreated bio-oil and VGO is introduced into the riser reactor from the feed vessel with the pump P-51.

liquid product recovery system includes a 3-m long air-cooled heat exchanger and a liquid product stabilizer. Detailed description of the unit along with analytical procedure followed to characterize the products is given in [15].

2.2. The FCC small-scale pilot plant unit

The CPERI FCC small-scale pilot plant unit (Fig. 2) operates in a full catalyst circulation mode with continuous regeneration and consists of a riser reactor (7 mm ID and about 9 m height), a stripper, a lift-line and a fluid bed as the regenerator system (78 mm ID). The catalyst circulation is achieved with two slide valves and is controlled in a similar way with a commercial FCC unit. There is an independent temperature control over several reactor zones, which allow isothermal operation for the entire system. Steam is used at the bottom of the stripper vessel for catalyst stripping. The separation of the gas and liquid products takes place using a specially designed refrigerated stabilizer. The liquid products, mainly C_5 and heavier, are condensed and collected. The pilot plant is fully automated and its process control system is based on a special industrial control system. The coke, the flue, the cracked gases and the total liquid product yields are measured in each FCC pilot plant test. From the total liquid product, gasoline, light cycle oil (LCO), heavy cycle oil (HCO) yields are determined using GC simulation distillation method (ASTM D2887). The produced cracked gases, the flue gases and the liquid products are measured with accuracy using a system of GC's, wet test meters and weight balances.

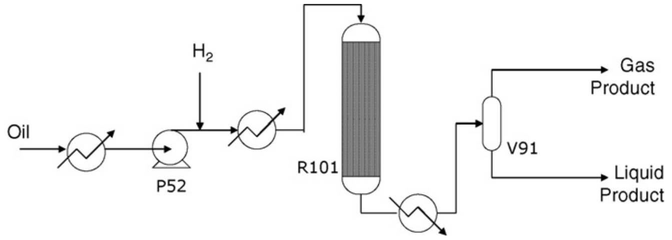

Fig. 3. Schematic diagram of the CPERI hydroprocessing pilot plant unit. P52 is the pump of the liquid feed, R101 the reactor and V91 the gas/liquid separator.

2.3. The hydroprocessing small-scale pilot plant unit

The CPERI hydroprocessing unit, depicted in Fig. 3, is a small-scale pilot plant unit which is employed for hydrotreating (HDS, HDN) and hydrocracking of various feedstocks, varying from light gasoil to heavy vacuum gas oil. It consists of a feed system, a reactor system and a product separation system. The feed system effectively maintains constant feed quality and H_2-to-oil ratio via a liquid feed pump and gas flow controllers. The reactor system consists of a single fixed-bed reactor ($L = 70$ cm, ID = 14.7 mm) with six independent heating zones which sustain the desired temperature profile within the reactor. The reactor product passes through the product separation system, where it is first cooled via a cooling zone and then flashed via a high-pressure low-temperature (HPLT) separator. The gas product flow enables the system pressure control via a pneumatic control valve. The liquid product flow is controlled via a separator level control system through a second pneumatic valve right after the HPLT separator. The liquid product is collected and several analyses can take place in the analytical laboratory of CPERI. The total liquid product are properties such as density, total sulfur, total nitrogen, carbon, hydrogen, bromine number and SimDist are of particular interest. Regarding the gas product, regular offline GC analysis provides information about the consistency of the gases product quality.

3. Experimental results and discussion

3.1. Biomass catalytic pyrolysis using FCC zeolitic catalysts

3.1.1. Materials

A forestry residue biomass (from beech wood) was used in this study for the pyrolysis (conventional and catalytic) experiments. The stoichiometric analysis of biomass in a dry basis (wt%) was: C = 49.41, H = 6.73, N = 0.16, O (by difference) = 42.96, ash = 0.54 wt%. The moisture content of the biomass was 8.25 wt%,

Table 1
Biomass fast pyrolysis results with two different heat carriers (S/B = 16)

	$T = 450\ ^{\circ}C$		$T = 500\ ^{\circ}C$	
	Silica sand	FCC	Silica sand	FCC
Raw product yields (wt% on biomass)				
Bio-oil yield	73.6	49.1	74.0	46.5
Gas yield	11.1	17.8	13.7	23.3
Char yield	10.4	22.9	7.1	22.4
Raw mass Balance	95.1	89.8	94.9	92.2
Individual liquid yield (wt% on biomass)				
Organic	55.9	18.3	57.3	16.2
Water	17.7	30.8	16.7	30.3
Individual gas yield (wt% on biomass)				
CO_2	6.9	8.5	7.0	9.8
CO	3.9	8.2	5.9	11.0
$C_1 + C_2$'s	0.3	0.5	0.8	1.0
wt% on organic bio-oil				
Hydrocarbons	5.0	7.4	5.5	7.5
Heavy oxygenates	36.2	18.3	30.1	10.8
Unidentified	23.3	12.9	20.1	19.1

while the gross heating value (GHV) was 18.22 MJ/kg. As heat carrier medium for the non-catalytic experiments, silica sand (particle size range: 100–250 μm, bulk density: 1.56 g/ml) was used, while an equilibrium FCC catalyst (particle size range: 50–180 μm, bulk density: 0.96 g/ml, TSA: 178.4 m^2/g, ZA: 58.5 m^2/g, UCS: 24.26 Å, Ni: 150 ppm, V: 367 ppm) was used for the catalytic tests.

3.1.2. Biomass catalytic pyrolysis results

All biomass pyrolysis experiments (both catalytic and non-catalytic) were performed at two different pyrolysis temperatures (450 and 500 °C) at a constant solid/biomass ratio of about 16. This means that the feed rate of the heat carrier was 16 times higher than the feed rate of the biomass. The flow rate of the inert nitrogen in the riser reactor was 4 l/min resulting in a vapor residence time in the riser reactor of about 1 s. The biomass feed rate was 0.6 kg/h.

The total liquid product yields obtained from the present experimental system, using silica sand as heat carrier, were in the range of 65–78 wt% (on biomass feed basis) depending on the experimental conditions and the type of feedstock [15]. These liquid yields are among the highest reported in literature for fluid bed pyrolysis units [2,3,30,31] and are attributed to some good characteristics of the unit like rapid mixing of biomass with the heat carrier medium, short residence time of the produced vapors in the riser reactor and rapid vapor quenching in the product recovery section. In Table 1, the experimental results at the two pyrolysis temperatures of 450 and 500 °C from the conventional biomass pyrolysis tests (using silica sand as heat carrier) are compared with those from catalytic pyrolysis (using the FCC catalyst as heat carrier). All tests were carried out with the beech wood biomass, the properties of which ere described above. From Table 1 it seems that the liquid production decreases while the gas and coke and char production increase considerably, when FCC catalyst is used instead of silica sand. These results are valid consistent for both temperatures and indicate that the FCC catalyst strongly favors the secondary reactions that lead to bio-oil decomposition.

Table 1 shows that at 450 °C the total gas and char yields are 11.1 and 10.4 (wt% on biomass basis), respectively, when silica sand is used. However, when temperature increases the gas yield increases while the char yield decreases. The increase of the total gases following an increase in temperature is attributed to the higher conversion rates of primary pyrolysis reactions (resulting in a lower char yield as listed in Table 1) and not in secondary cracking reactions. The effect of temperature increase is more significant when the FCC catalyst is present. This happens especially for gases (Table 1), where the oxygen compounds (CO, CO_2) dominate. At 450 °C and with the silica sand, CO_2 was the component with the highest yield (6.9 wt% on biomass basis) while CO was the second highest (3.8 wt% on biomass basis). However, even at a small temperature increase of 50 °C, CO_2 remains the same, while CO increases rapidly reaching yields around 6 wt%. This is because mostly CO_2 is produced by carboxyl groups which are easily decomposed at relatively low temperatures. On the contrary, CO is formed by cracking the most stable carbonyl groups and thus, higher temperatures are required for higher productions [32]. All these results regarding the effect of temperature on product yields are in agreement with results reported in literature [31]. The cracking of the stable carbonyl groups are much more pronounced when the FCC catalyst is present. Thus, while in the 450 °C the CO is around 5 wt% in the 500 °C it reaches values of about 10 wt%. This means that this catalyst favors the decarbonylation reactions that lead to more CO.

Catalysts, however, radically affect the bio-oil characteristics apart of its yield. The quantitative and qualitative analysis of the organic bio-oil was based on a GC/MS system (HP 5989 MS ENGINE with electron energy 70 eV; emission 300 V; helium flow rate: 0.7 cc/min; column: HP-5MS) [15]. From this analysis it was shown that the bio-oil with the FCC catalysts contains more hydrocarbons (Table 1) and much less heavy oxygenated compounds (Table 1) compared with thermal bio-oil (from the silica sand). This is attributed to the cracking of heavy compounds into lighter one, in the presence of the acidic FCC catalyst (deoxygenating reactions). However, these reactions lead mainly to water (Table 1) and thus the water content of the catalytically produced bio-oil is around 60 wt% much higher to that in the conventional (thermal) bio-oil (with the silica sand) which was 24 wt% at 450 °C and 22.6 wt% at 500 °C. In the literature a wide range of water contents in thermal bio-oils has been reported (15–30 wt%) depending on the type of feedstock and process conditions [3,7,12]. The presence of water changes significantly the physical properties of the bio-oil produced from the FCC catalysts [33]. These properties (based on ASTM measurements) are listed in Table 2 (for the experiments at 450 °C) and are compared with the properties of the thermally produced bio-oil. The density of the thermal bio-oil was 1.19 g/cm^3 while that of the catalytic one about 1.0 g/cm^3. The presence of catalyst reduces also the micro-carbon residue tester (MCRT) of the bio-oil which is an indication of heavy oxygenated components. The presence of water in bio-oil is responsible for its low-calorific value (GHV) as indicated in Table 2.

From all the above results it appears that the presence of catalyst can change the quality and yield of the bio-oil produced from a catalytic pyrolysis process. Of course the FCC catalyst is a very active one producing mainly water and coke and thus, it does not seem an appropriate catalyst for this application. More

Table 2
Physical properties of bio-oils produced from silica sand and FCC catalyst ($T = 450\ ^{\circ}C$, solid/biomass = 16)

Property	Silica sand	FCC
Density at 15.6 °C (g/cm^3)	1.19	1.00
Viscosity at 50 °C (cSt)	6.3	1.0
Viscosity at 50 °C after heating for 6 h at 80 °C (cSt)	8.5	2.4
Viscosity at 50 °C after heating for 24 h at 80 °C (cSt)	10.8	3.4
Conradson carbon residue (MCR) (wt%)	16.2	1.8
Pour point (°C)	−33	−19
Flash point (°C)	62	37
HHV (MJ/kg)	16.3	7

Table 3
Properties of the two fractions produced after thermally hydrotreating the bio-oil

Property	Light fraction	Heavy fraction
Elemental analysis (wt%)		
C	82.2	84.4
H	10.7	9.4
S	0.01	0.01
N	1.15	0.42
O	6.4	4.9
H_2O (wt%)	0.99	–
Density (g/cm^3) (15 °C)	0.942	1.036
Distillation (°C, wt%)		
<200	27	
200–350	55.3	23
350–500	17.8	66
>500		11

research is needed to identify a more suitable catalyst for the suggested process.

3.2. Upgrading the biomass fast pyrolysis liquids (BFPLs)

The upgrading of BFPL to transportation fuels by using a hydrotreating technology was studied in CPERI in collaboration with veba oil. This technology was applied in two different modes: a catalytic one using conventional hydrotreating catalysts and a thermal one without any catalyst. The detailed results from this study are presented in reference [24]. Based on this work, the catalytic hydrogenation of bio-oil faced many operating problems due to plugging of the catalyst bed, however it can achieve very high-de-oxygenation conversion (higher than 85% wt). On the contrary the thermal hydrogenation of bio-oil was proved to be feasible and without operational problems. With the thermal hydrogenation of bio-oil up to 85 wt% de-oxygenation conversion was achieved, producing hydrotreated oil with oxygen content of about 6.5 wt%. The yield of the hydrotreated bio-oil was about 42 wt% (based on the non-hydrotreated bio-oil). Due to the low-oxygen content of the thermally hydrotreated bio-oil (6.5 wt%), it can be separated by distillation in a light (LBFPL) and a heavy fraction (HBFPL) with the characteristics presented in Table 3. From the distillation data of Table 3 it seems that the light fraction comprised of components mainly in the gasoline and diesel range and thus, it could be blended directly with the corresponding petroleum fractions. The heavy fraction (HBFPL) has characteristics similar to conventional VGO. This heavy fraction could be used as co-feed with vacuum gas oils (VGO) in the FCC process of a conventional refinery and to play the role of resid in the feedstock of the FCCUs. The bio-oil co-processing technology proposed by CPERI is presented schematically in Fig. 4.

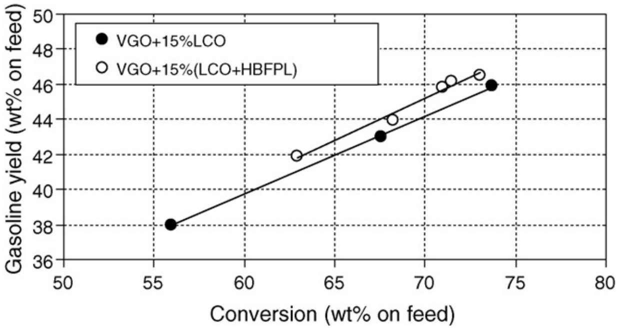

Fig. 5. Gasoline yield from co-processing hydrotreated bio-oil (HBFPL) with VGO in the FCC pilot plant.

In the present paper the above concept is supported further by using the thermally hydrotreated heavy bio-oil fraction (Table 3) as co-feed with conventional VGO in the FCC unit. For this reason, experiments in the CPERI FCC small-scale pilot plant unit were performed using as feedstock a blend of the above heavy hydroteated fraction with conventional VGO. The main problem with such feeds is the plugging of the nozzle of the FCC small-scale pilot plant. In order to overcome this problem, the HBFPL was diluted in light cycle oil (LCO) in a portion 15/75 by weight and the mixture was finally blended with a conventional FCC feed (VGO). The properties of the VGO (supplied by a Greek refinery) were: density (60 °C) = 0.874 g/cm^3, S = 0.165 wt%, MCRT = 0.2 wt%, MeABP = 464 °C. The total mixture of the LCO + HBFPL was 15 wt%. For a direct comparison of the effect of bio-oil in the FCC base case tests were initially performed, using as feed VGO + 15% LCO and tests with the mixture of VGO + 15% (LCO + HBFPL). All experiments were carried out in an isothermal riser operation of 520 °C and a partial pressure of hydrocarbons in the riser of 12 psia. The nitrogen flow rate in the riser was 3500 cc/min and the residence time of the vapors in the riser was 0.8 s. The main variable of the unit was the C/O ratio by changing the feed preheat in order to achieve different conversion levels. The catalyst used was a Ecat of the same Greek refinery with properties: TSA = 158 m^2/g, RE = 0.65 wt%, Ni = 163 ppm, V = 362 ppm. The pilot plant performance during the tests was satisfactory and without any operating problem (nozzle plugging) during the injection of the bio-oil into the unit. The total mass balances of the tests were in the range of 98–101 wt%.

The experiments results of this study are presented in Figs. 5–7 for some key FCC products. Figs. 5 and 6 shows that the VGO/HBFPL co-feed produces about 1 wt% more gasoline and more LCO compared to the VGO feed. Obviously the hydrotreated bio-oil (HBFPL) components favored cracking into gasoline and diesel

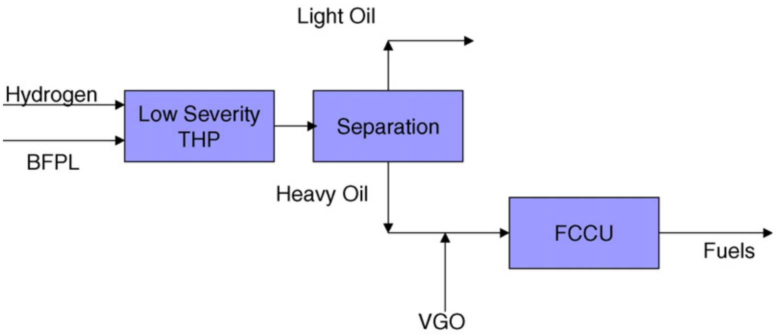

Fig. 4. Bio-oil co-processing technology investigated in CPERI. The heavy oil from the low-severity hydrotreating process of the bio-oil is introduced to the FCC after mixing with conventional VGO.

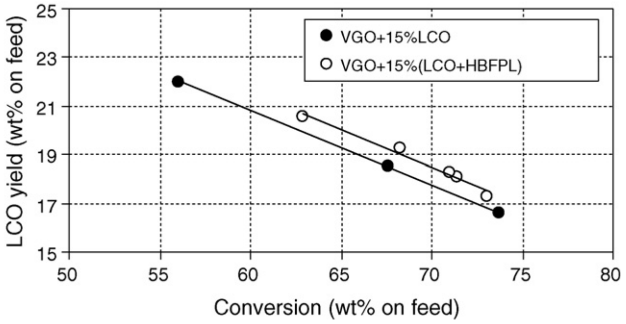

Fig. 6. LCO yield from co-processing hydrotreating bio-oil (HBFPL) with VGO in the FCC pilot plant.

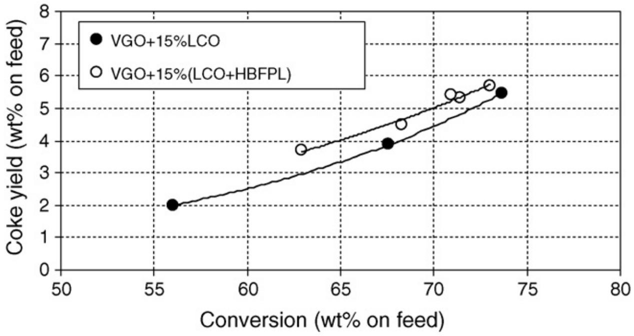

Fig. 7. Coke yield from co-processing hydrotreating bio-oil (HBFPL) with VGO in the FCC pilot plant.

components. Of course as we expected the coke is higher (about 0.5 wt%) with the co-feed (Fig. 7) compared with the VGO. However, this increase is affordable for the FCC process. On the contrary to the previously described products, all LPG gas yields are lower when bio-oil is added in the feed (not presented in figures). Regarding the quality of the gasoline, PIONA analysis showed (not presented in figures) that the gasoline produced when bio-oil is present contains more aromatics and less paraffins and olefins compared to the gasoline with no bio-oil. The experimental results also showed that the presence of bio-oil in VGO reduces the crackability of the feedstock (not presented in figures). Thus, at the same C/O ratio the conversion was reduced about 1 wt% when the heavy hydrotreated bio-oil (HBFPL) was present. This is explained by the fact that the HBFPL contains heavy components not easily crackable. These components require more catalyst to be cracked. However, as it was described above, the selectivity of some FCC products is favored by the presence of HBFPL.

The above described tests showed that the suggested option of co-feeding a petroleum VGO with a thermally hydrotreated bio-oil (HBFPL) is technically viable for FCC units running with good quality feedstocks (and thus having excess coke burning capacity).

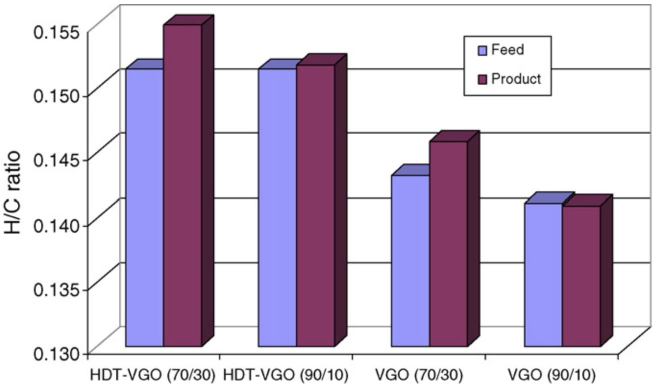

Fig. 8. Feed and product hydrogen-to-carbon ratio (H/C) of co-hydroprocessing VGO (hydrotreated and non-hydrotreated) + sunflower oil.

Certainly further investigation is needed for this option regarding mainly the effect of bio-oil concentration (as co-feed) on FCC product yields and selectivities.

3.3. Co-hydroprocessing of VGO and sunflower oil

As it was mentioned in the introduction, vegetable oils can also be used as an alternative feedstock in conventional refining processes. In this study co-hydroprocessing of VGO–sunflower oil mixtures was explored as another potential technology for biofuels production.

Four different feedstocks were utilized as the basis of this study. The first two feedstocks were mixtures of pre-hydrotreated VGO (HDT-VGO) with sunflower oil at a 70/30 and 90/10 (v/v) ratio. The other two feedstocks were mixtures of straight run VGO (not hydrotreated) with sunflower oil at a 70/30 and 90/10 (v/v) ratio. The main properties of the four feedstocks appear in Table 4. For the two feedstocks containing hydrotreated-VGO, dimethyl-disulfide (DMDS) and tetra-propyl-amine (TPA) were added in order to regulate the catalyst activity, since sulfur and nitrogen levels were very low after the initial pre-hydrotreatment.

All hydroprocessing experiments were conducted at constant conditions which were the same for all experiments ($T = 350\ ^{\circ}\mathrm{C}$, $P = 2000$ psig, LHSV = $1.5\ \mathrm{h}^{-1}$, $F_{\mathrm{L}} = 20$ ml/h, $F_{\mathrm{G}} = 0.75$ scfh), simulating actual operating conditions of commercial hydrotreating processes. Furthermore the same noble metal mild-hydrocracking catalyst was employed in all four experiments. The main properties (density, carbon, hydrogen, total sulfur, total nitrogen, bromine number and simulated distillation) of the four co-hydroprocessing experiments liquid products were analyzed once the process reached steady state. The oxygen content was estimated as the remaining element ($100 - \%\mathrm{C} - \%\mathrm{H} - \%\mathrm{S} - \%\mathrm{N}$).

Hydroprocessing allows the catalytic hydrogen addition to heavy hydrocarbon molecules. Hydrogen allows the saturation of

Table 4
Feedstock properties for co-hydroprocessing of VGO and sunflower oil

	Hydrotreated VGO + sunflower oil		Non-treated VGO + sunflower oil	
	70/30	90/10	70/30	90/10
Density (kg/m^3)	0.8667	0.8578	0.8910	0.8935
Sulfur (wppm)	16,910	18,600	16,030	19,810
Nitrogen (wppm)	532.1	662.16	792.87	998.7
Hydrogen (wt%)	12.396	12.725	11.873	11.868
Carbon (wt%)	81.85	84.02	82.90	84.10
Oxygen (wt%)	4.01	1.33	3.54	1.95
Bromine no.	21.31	7.95	21.08	

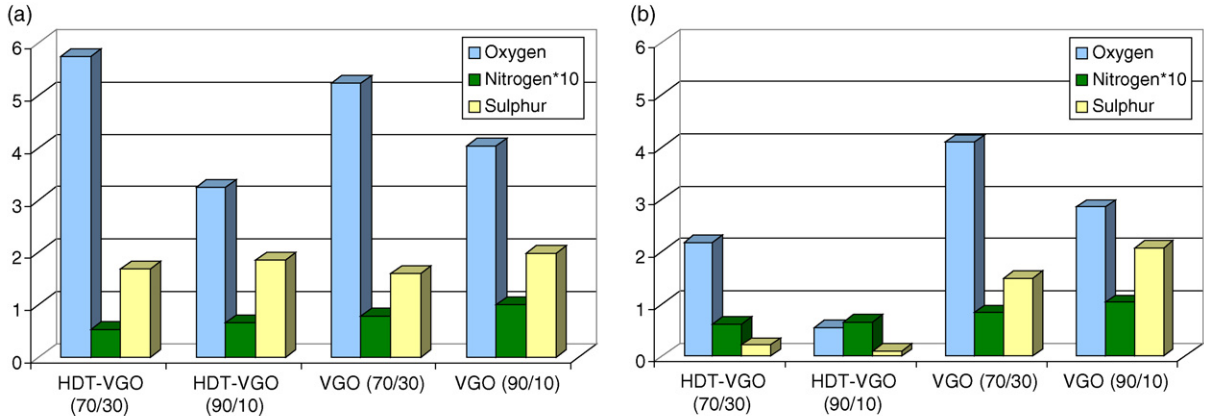

Fig. 9. Heteroatoms (O, N, S) content of the feed (a) and product (b) in the co-hydroprocessing of VGO with sunflower oil.

unsaturated bonds, heteroatom (mainly S, N and O) removal as well as isomerization and cracking. The effect of co-hydroprocessing of the four VGO–sunflower oil feedstocks is shown in Fig. 8, as expressed in the change of hydrogen-to-carbon ratio (w/w). In the case of the HDT-VGO + sunflower oil feedstocks the H/C ratio was larger, as expected, since the contained fossil stream (HDT-VGO) was already hydrotreated before being introduced with the sunflower oil. Another interesting conclusion was that the increase of H/C ratio was much larger for the two feedstocks with higher amounts of bio-component (70/30), indicating that co-hydroprocessing primarily affects the heavy hydrocarbon molecules of the sunflower oil component of the feedstock mix.

In terms of heteroatom removal, the results are summarized in Fig. 9. Feed properties, as compared in Fig. 9(a), appear similar for all four feedstocks, except for the oxygen content, which is larger for the two feedstocks with the higher sunflower oil content (70/30). Comparing Fig. 9(a) and (b) one can conclude the effectiveness of heteroatom removal. First, oxygen removal is more effective for the two hydrotreated VGO + sunflower oil feedstocks than for the two non-treated VGO + sunflower oil feedstocks. Regarding sulfur removal, it was only achieved in the case of the two pre-hydtrotreated VGO + sunflower oil feedstocks, while it appeared negligent for the non-treated VGO + sunflower oil feedstocks. This is actually expected as sulfur contained in the non-treated VGO was in the form of mercaptanes, sulfides, benzothiophenes, and thiophenes which can only be removed using a catalyst specialized in HDS/HDN. Finally nitrogen removal remained relatively unaffected.

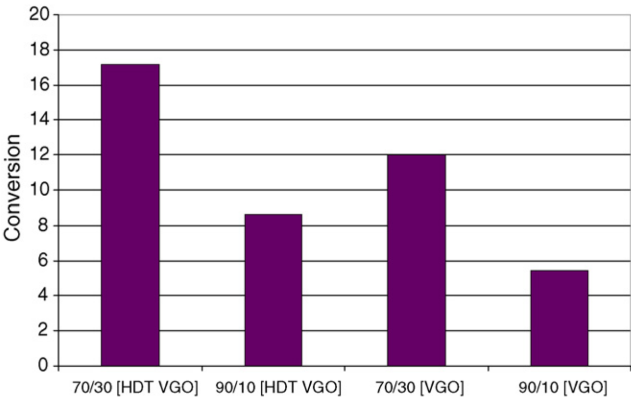

Fig. 10. Conversion of co-hydroprocessing hydrotreated and non-hydrotreated VGO.

A well-accepted measurement indicating the effectiveness of hydrocracking is *conversion*, which is defined as follows:

$$\text{Conversion} = \frac{[\text{Feed}\ \ 360+\ \ (\text{wt\%})] - [\text{Prod}\ \ 360+\ \ (\text{wt\%})]}{[\text{Feed}\ \ 360+\ \ (\text{wt\%})]} \times 100$$

where [feed 360+ (wt%)] and [Prod 360+ (wt%)] is the wt% of the feed and product which boils over 360 °C, calculated from the distillation curves of feed and product, respectively.

The conversion of the four co-hydroprocessing experiments in Fig. 10 indicates that hydrocracking conversion of VGO–sunflower oil mixtures is not as high as the conventional hydrocracking conversion of VGO (60–80%). The presence of sunflower oil appears to inhibit hydrocracking conversion, as it was smaller for the two feedstocks with larger sunflower oil amounts (70/30). Moreover hydrocracking appears to be greater for pre-hydrotreated VGO–sunflower oil feedstocks rather than for non-treated VGO + sunflower oil feedstocks.

4. Conclusions

In this work small-scale pilot plant results are presented from the upgrading of various bio-based liquids through existing refining processes. Initially the process of biomass catalytic pyrolysis was investigated using an FCC catalyst. The results showed that this catalyst gives a lower bio-oil yield but with an improved quality. However, in general it seems that this process has a lot of potential when an appropriate catalyst is used. Of course more research is needed on this issue. The co-processing of gas oil with a thermally hydrotreated bio-oil was also investigated in this paper. The results showed that the presence of the bio-oil favors the gasoline and diesel production but increases the coke yield. However, depending on the concentration of biomass liquids, it was shown that this option is technically viable for FCC units running with good quality feedstocks, that is the FCC unit with excess coke burning capacity. Finally the co-hydroprocessing of VGO (hydrotreated and non-hydrotreated) with sunflower oil (in two different concentrations) was studied. The results showed that the presence of sunflower oil inhibits hydrocracking conversion (especially when non-hydrotreated VGO was used), however, this upgrading option is feasible producing a good quality diesel.

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