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Perspective on Co-feeding of Phenolic Compounds into Existing Refinery Units

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Abstract

Replacement of fossil materials by renewable feedstocks is forced by depletion and environmental concerns but requires new technologies for energy generation or production of chemicals. Co-processing of petroleum with renewable feedstocks in current refinery infrastructure is an attractive option in the mid-term to increase renewable fuel capacity, as the capital investment and operational costs would be marginal. In this chapter, various strategies for admixing of phenolic compounds as renewable feeds into standard refineries are described. Starting from the role of renewable resources (e.g. biomass, lignin and bio-oil) in the current and future energy and chemical community, an overview on the present energy supply situation and the role of phenolic compounds are discussed. Later, a summary on co-feeding of phenolic model compounds with conventional feeds in refineries are illustrated. The co-processing of upgraded bio-oil in refinery units [e.g. fluid catalytic cracking (FCC), hydrotreating] is summarized, showing the potential utilisation of bio-feeds via such processes. Finally, some concluding remarks address the perspectives for further research and development to overcome future challenges.

Keywords: bio-feeds, bio-oil, co-feeding, lignin, refinery

1. Introduction

Fossil fuel (e.g. crude oil, coal and natural gas) reserves are limited, but they still share a significant proportion in the worldwide energy consumed (i.e. more than 85% in 2014). Particularly, 86% and 81% of primary energy in the US and Germany are from those sources in 2014, respectively [1]. A minor portion stems from other resources (e.g. nuclear and hydroelectric power, wind, solar, geothermal and biomass) [2]. The current share of renewable feedstock supplied to chemical industry looks similar, e.g. only 8–10% of the raw materials of the

European chemical industry are bio-based. It is projected that energy demand increases in the coming decades in spite of improved energy efficiency. Power plants based on photovoltaics and wind energy will continuously emerge for primary energy supply. At the same time, demand for transportation fuels will grow, but the production of renewable fuels is an even more challenging task. No single renewable source can provide sufficient energy to close the gap between the supply and demand of energy.

Another driving force for replacing petroleum-derived liquid fuels is the concerns about environmental pollution, as the production and combustion of fossil fuel add more CO₂, SO_x and NO_x to the atmosphere. Hence, there is a strong motivation for research on alternatives for fossil fuels. Many researchers have recently turned attention to the massive biomass resources due to several reasons. First, some types of biomass like vegetable oils already fit quite well into the present carbon-based fuel infrastructure. Second, biomass production is based on short-time carbon cycles and overall CO₂ neutral. Additionally, biomass is a cheap, abundant and sustainable raw material. Moving the world market dependence away from fossil-based resources to renewable ones will definitely contribute to the climate protection and sustainable economy [3–5].

Current production of first-generation biofuels (e.g. bioethanol and biodiesel) and blending in conventional fuels up to 10 vol% are steps in the right direction. However, the use of edible oils and seeds for the biofuels might compete with the food value chain, affecting material availability and prices. Furthermore, only part of biomass is converted into fuels. Consequently, the next step aims at the utilisation of complete biomass, leading to second-generation biofuels. The access to biofuels from biomass resources offered by forestry, agriculture and industry have great potential for the production of fuels and chemicals [6]. As a result, the governments of many countries have set ambitious goals and set the mandatory legislation for partly replacing fossil fuels to promote the implementation of renewable energy, e.g. the U.S Department of Energy sets a target to expect use 20% of transportation fuel from biomass.

The three most important plant biomass constituents are as follows: (i) cellulose, a polymer of glucose; (ii) hemicellulose, also a polymer of different sugars; and (iii) lignin, a highly aromatic polymer consisting of an irregular array of variously hydroxyl- and methoxy-substituted phenylpropane units. Such biomass has low volumetric and energy densities, resulting in high costs for collecting and transportation. As a result, converting biomass either chemically or thermally into liquid crudes is necessary as a first step. Fast pyrolysis (FP) or liquefaction (LF) seems to be potential technologies for liquefying biomass. Usually, such crudes possess oxygen contents varying in a range of 35–45 wt%, which has to be lowered prior to any use as a transportation fuel. Otherwise undesired properties like low specific energy content or limited shelf life will be serious drawbacks for application as fuels compared to conventional fuels.

Fortunately, the processes for upgrading such crudes already exist. Petroleum industry is mature all over the world and the use of the existing infrastructure (e.g. storage, refining units, blending and distribution systems) for production of biofuels requires little capital investment cost. As a result, research and development of the co-processing of biomass-derived feeds

into refinery have been proposed. Three insertion points have been proposed: (i) feeding into crude oil before the crude distillation units; (ii) blending in near finished fuel and (iii) feeding into facilities within the refinery. The first option might be ruled out as the separation in distillation units does not chemically alter the materials and the oxygen-containing contaminants would be spread throughout the refinery. The second option requires converting the biomass into blending components which must meet all standards for transportation fuels. This is really challenging and needs higher costs. The last option receives more and more attention from academia and industrial partners, as various material streams are usually processed in a refinery and different bio-crudes with similar properties can be fed to the most suited unit operation.

This book chapter summarizes the main aspects involved in the co-feeding of liquefied lignocellulosic biomass feedstock based on phenolic compounds together with conventional hydrocarbon feeds into standard refinery units.

2. Overview of bio-feeds and conventional feed for standard refinery

Bio-feeds can be generally categorized based on the following sources: (i) food crops such as corn, wheat, barley, sugar crops, vegetable oils and hydrocarbon plants; (ii) waste materials such as agricultural residues, wood, urban wastes and crop residues; and (iii) aquatic biomass such as algae and seaweed. The use of biomass-derived feedstocks for a petroleum refinery can be classified into three categories according to the sources: lignocellulosic biomass, starch- and sugar-derived biomass (or edible biomass) and triglyceride-based biomass. There are several issues to identify what kind of bio-feeds is suited for refinery, among which price, availability and conversion costs play important roles. Generally, the cost of biomass increases in the order: lignocellulosic biomass < starch (and sugar)-based biomass < triglyceride-based biomass. However, the investment cost of conversion technology raises in the reverse order [7]. Naturally, the cost is also linked to supply and demand and thus finding new uses for biomass-derived products will result in higher prices.

For comparison between renewable and fossil feeds, hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C) atomic ratios are generally evaluated. Particularly, H/C ratios of crude oil are typically between 1.6 and 2.1 and the O/C ratios range between 0 and 0.03. In contrast, wood-based biomass typically has O/C and H/C ratios higher than 0.61 and 1.4, respectively. Of the biomass components, lignin is markedly different in structure and composition from hemicellulose and cellulose, being highly aromatic and containing less oxygen and is thus the one most similar to petroleum. Lignin has lower O/C and H/C ratios compared to wood-based biomass and thus making it to be a potential source for fuels production [8]. Naturally, lignin is a cross-linked macromolecule and consists of three basic monomers such as p-coumaryl alcohol, coniferyl alcohol and synapyl alcohol. Lignin from softwoods is mostly made-up of coniferyl alcohol-derived components, but lignin from hardwoods consists of mixtures of coniferyl- and syringyl-derived structures. Nowadays, the utilisation of lignin is continuously growing. Large amounts of lignin and lignin containing residues originate from the pulp and paper industry. The expected growth of the production capacity of second generation biofuels

(e.g. bioethanol) from lignocellulosic biomass will lead to another source of lignin and lignin containing residues.

It should be highlighted that the complex nature of lignin polymer and its stability make it difficult to convert it into valuable monomeric chemicals. As mentioned above, FP or LF is widely used to convert biomass or lignin into liquid bio-crude or bio-oil. Under these conditions, biomass is converted into more than 200 oxygenated compounds, having various types of functional groups (e.g. acids, alcohols, phenols, sugars, aldehydes, ketones and esters) with specific chemistry. Lignin is preferably converted into phenolic compounds such as phenol, anisole, guaiacol, cresol and syringol. These compounds are highly recalcitrant to further treatment and require severe reaction conditions. As a result, such phenolic compounds have attracted attention as model compounds to develop effective treatment processes. **Figure 1** illustrates the structure of the three main biomass components and a variety of commonly detected monomeric oxygenates in bio-oil; in addition, phenolic dimers are also represented largely in lignin-derived bio-oil [9].

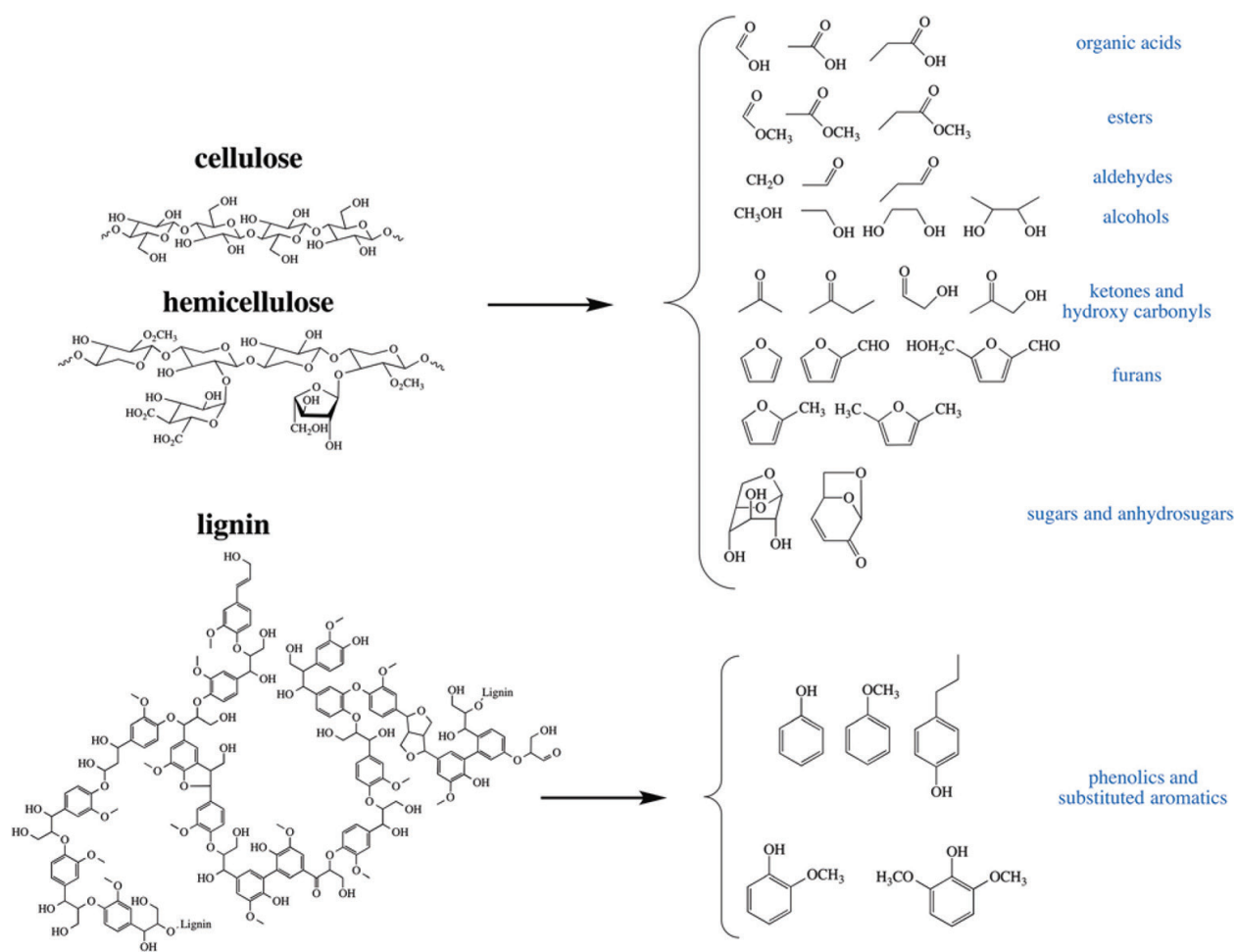


Figure 1. Typical products formed from FP of lignocellulosic biomass. Adapted from Ref. [9].

Details on the nature of conventional petroleum feeds and a block scheme of a typical refinery are presented elsewhere [10]. It should be noted that there are five major types of hydrocarbons in petroleum feedstocks such as paraffins, iso-paraffins, aromatics, naphthenens and olefins (PIANO). The main objective of refineries are (i) to transform crude oil into a set of refined products in accordance with precise specification and in quantities corresponding as closely as possible to the market requirement. For specific purpose, crude oil is first fractionated (distilled) into fractions with a specified range of carbon number. Following that, such large fractions (referred to gas oil and residue) are further processed in order to reduce molecular weight and to increase the H/C ratios.

It is suggested that refineries are well-suited to handle FP oil or phenolic compounds, in particular. However, the significant difference in the quality of biomass-derived liquids and petroleum feeds are obvious. For example, FP oil reveals a general sum formula of $\text{CH}_{1.4}\text{O}_{0.6}$ in contrast to hydrocarbon fuels, showing a sum formula close to CH_2 . In addition, the higher heating values of FP or LF oils amount to approximately 16-34 MJ/kg, in contrast to heavy fuel oil that offers 40 MJ/kg (**Table 1**).

The different properties definitely cause some problems [9]: (i) the high oxygen content is not accommodated by refineries, usually dealing with oxygen contents in the crude oil far below 1 wt%; (ii) oxygenated compounds typically have higher boiling points than hydrocarbon with the same carbon number; (iii) water is considered a contaminant in conventional refineries; (iv) the acidity of FP oil is much higher than that of crude oil; and (v) the presence of various reactive oxygen-related functionalities allows thermal polymerization and might subsequently cause a high coking rate.

Therefore, downstream removal of the remaining oxygen from the bio-crude is needed; this can be done by using the existing refinery infrastructure or standalone units [12, 13]. Among

Properties	FP oil	LF oil	Heavy fuel oil
Water content (wt%)	15–30	5.1	0.1
pH	2.5	–	–
Specific gravity ^a	1.2	1.1	0.94
Elemental composition (wt%)			
Carbon	54–58	73	85
Hydrogen	5.5–7.0	8	11
Oxygen	35–40	16	1.0
Nitrogen	0–0.2	–	0.3
Ash	0–0.2	–	0.1
HHV (MJ/kg)	16–19	34	40

^[a] Ratio of the density of the substance to the density of water.

Table 1. Typical properties of wood-based bio-oil (via FP, LF) compared to heavy fuel oil. Adapted from Ref. [11].

the available upgrading strategies, fluid catalytic cracking (FCC), hydrotreating, and hydrocracking supported by catalysts are considered as most effective technologies provided by the refinery [14–16]. However, these unit operations are tuned to upgrade fossil fuels. On the other side, recently developed standalone processes are definitely tailored to lower the oxygen content in biocrudes most effectively. They are often discussed as deoxygenation or hydrodeoxygenation (HDO) processes. A detailed review on the deoxygenation of liquefied biomass and related model compounds in standalone units have been reported in Ref. [17]. The focus of the present review is now set on the co-feeding of phenolic model compounds with hydrocarbons and later on blending of (pre-treated) bio-crudes with conventional refinery feeds. This latter strategy might represent a kind of third way, tailoring the bio-crudes to make them suited co-feeds and to benefit from existing technology.

3. Co-feeding of model compounds into existing refinery units

Several options are available for converting oxygen-containing biomass-derived feeds into bio-fuels in a petroleum refinery: (i) thermal conversion (e.g. visbreaker and coker); (ii) catalytic conversion (e.g. FCC, hydrotreating and hydrocracking) [18].

Nevertheless, the obtained organic liquid product from thermal units would contain a high fraction of oxygenates and thus those units seem to be unsuitable choices. In contrast, in presence of catalyst (FCC unit), catalytic cracking is much faster and more selective than thermal cracking and it allows working under milder reaction conditions.

The main objective of hydrotreating in conventional refineries is to remove impurities (e.g. sulphur, nitrogen and oxygen) being present in petroleum feedstock via the addition of hydrogen (hydrodesulfurisation = HDS, hydrodenitrogenation = HDN). Therefore, hydrotreating is also expected to remove the high content of oxygenates in bio-feeds. Hydrocracking, on the other hand, combines hydrotreating and catalytic cracking, thereby transforming hydrocarbon feedstocks in the presence of hydrogen into lighter products. Hydrocracking typically is carried out using other catalysts than for hydrotreating, and is run at more severe operating conditions (higher temperatures and pressures).

3.1. HDO of co-feed of phenolic model compounds with hydrocarbon

The individual HDO of bio-oil and related oxygenated model compounds has been studied extensively. In the past, this process was considered to provide hydrocarbon fractions that might be blended directly with conventional fuels. However, this needs huge efforts to achieve the necessary hydrogenation depth and oxygen removal efficiency. Recently, it is often discussed as a pre-treatment (or upgrading) step to make bio-crudes suited for co-processing. Details are summarized in Ref. [17] and related reviews [2, 19]. We also studied the HDO of phenol and intermediates on monometallic and bimetallic Ni-based catalysts (Ni, Ni-Co, Ni-Cu) supported on different acidic materials (H-ZSM-5, H-Beta, H-Y and ZrO₂) at comparatively mild conditions (250°C, 50 bar initial H₂ pressure) [20, 21]. Hydrocarbons (e.g. cyclohexane and benzene) can be mostly produced from deoxygenation of phenol. Similarly, guaiacol and its derivatives, which possess hydroxyl and methoxyl groups attached to the

aromatic ring, have been investigated extensively as model compounds, e.g. Refs. [22, 23]. Various pathways have been reported for guaiacol conversion towards a variety of products such as phenol, catechol, benzene, cyclohexane, and methyl-substituted phenols. Such a reaction network for the guaiacol catalytic cracking has been proposed in Ref. [32]. Besides, phenolic dimers have been involved in HDO studies due to their large amount in lignin derived bio-oils. During the aqueous phase, HDO of phenolic dimers on bifunctional catalysts (Pd/C, H-ZSM-5, or Ni/H-ZSM-5) hydrocarbon yield were observed up to 95–100% at 64–100% conversion [24, 25].

Co-processing of guaiacol to straight-run gas oil (SRGO) was studied in a conventional hydrotreating process [26]. In the presence of SRGO and under severe HDS conditions, no inhibiting effect on HDS activity was observed; however, at mild reaction temperature (below 320°C) and low space velocity, inhibition of HDS became relevant, likely due to competitive adsorption of intermediate phenols on the catalyst active sites. By increasing the temperature, these adsorbates are rapidly deoxygenated into hydrocarbons which did not affect HDS reactions. Otherwise, hydrogen sulphide from HDS suppresses hydrogenolysis and hydrogenation (HDO) of phenols, especially with NiMo and CoMo catalysts, via competitive adsorption of phenol and H₂S [27]. Similarly, ammonia stemming from HDN not only depresses the activity of NiMo and CoMo catalysts in HDS process, but also the conversion of carboxylic and methoxy groups, while ketones were not affected [28]. The presence of other compounds, such as water, has little influence on HDO reaction but does affect the lifespan of HDS catalyst.

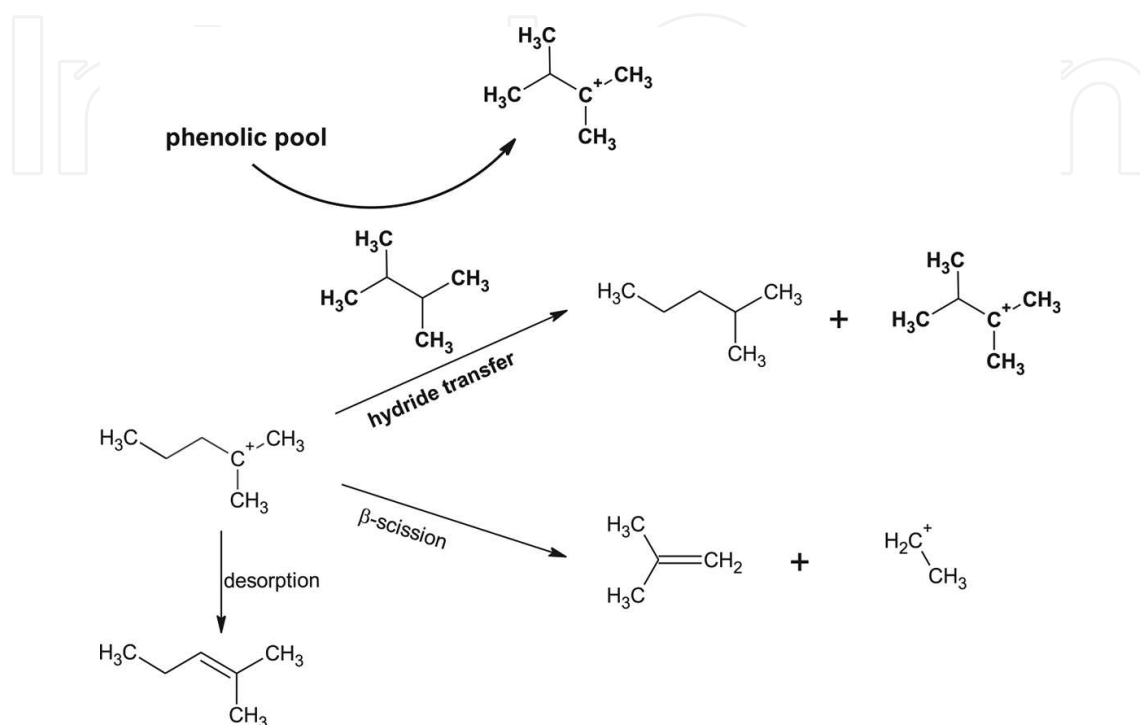
3.2. Co-feeding of phenolic model compounds with conventional feeds at FCC conditions

Co-processing of oxygenated model compounds with conventional feeds at FCC conditions has been studied in lab-scale FCC units [29–32]. A maximum amount of 10 wt% of oxygenated compounds (related to gasoil) could be fed to a FCC without major problems. Additionally, the authors indicated that catalytic cracking of oxygenate compounds consists of a complex net of reaction pathways.

Either phenol or guaiacol was co-fed with hydrocarbon (e.g. n-heptane or methylcyclohexane) for cracking reactions over HZSM-5 and HY zeolites [31]. The severe slow-down of the cracking reaction of methylcyclohexane and n-heptane was observed in the presence of the named oxygenates. The authors proposed the observation due to strong adsorption of phenolic species on the catalysts and thus it could be competitive with the absorption of hydrocarbon. The increased coke formation in the presence of phenolic compounds also led to a slightly changed product distribution compared with hydrocarbons cracking.

Co-feeding of oxygenates (including guaiacol, acetic acid, phenol and hydroxyacetone) with gas oil over an equilibrated FCC catalyst [32] lead to an increase in yields of fuels gas, liquefied petroleum gas (LPG) and gasoline, however, this was possible mostly because boiling point range of those oxygenates and their products match these fractions. Additionally, some aromatic products were obtained from dehydration and alkylation of both phenol and guaiacol in the gasoline fraction products.

Recently, it was shown that small amounts of *m*-cresol at low reactant concentrations caused fast deactivation of an FCC catalyst [33]. Nevertheless, increasing the paraffin concentration hindered the deactivating effect of *m*-cresol. The authors postulated a hydride transfer between the phenolic compound and the paraffins. The interaction of the phenolic pool and the conventional feed (paraffin) via hydride transfer is summarized in **Scheme 1**.



Scheme 1. Interaction of the *m*-cresol and paraffin transformation via hydride transfer. Adapted from Ref. [33].

In sum, the cited studies on co-feeding of phenolic model compounds with hydrocarbons give some insight (e.g. competitive adsorption and hydride transfer) that should be taken into account for the development of effective catalyst and revise the processes later on.

4. Co-processing of upgraded bio-oil as a phenolic feed into refineries

As mentioned above, bio-oils obtained from FP or LF of solid biomass have some peculiar properties (high oxygenate (35–50 wt%) and water content (15–30 wt%), high acidity and immiscibility with petroleum fuels) being different from those of conventional refinery streams [34]. Conversion of pure FP oil over conventional FCC catalysts has been studied already in the nineties [35, 36]. However, major challenges were identified (e.g. nozzle plugging and irreversible catalyst deactivation) owing to significant formation of coke, tar and char [37]. This leads to a more severe catalyst deactivation compared to regular FCC process. Thus, the direct use of an untreated bio-oil in standard refinery units needs large efforts in catalyst and process design that might make this route less attractive. Instead, blending of FP oil with conventional feed (e.g. vacuum gas oil) before introduction into FCC unit is the logical alternative due to the interest of petroleum oil companies.

The standard lab-scale techniques for evaluation of FCC catalysts [e.g. micro-activity test (MAT) or advanced cracking evaluation (ACE)] may also simulate the co-processing of FP oil with conventional FCC feeds. Such tests are known to elucidate the actual behavior of commercial FCC units quite well and various parameters [e.g. catalyst-to-oil (CTO) ratios, temperature, conversion and product distribution] can be systematically investigated. For example, UOP reported the first results for such blending tests in an ACE test unit [38]. **Table 2** provides typical results for pure vacuum gas oil (VGO) cracking in comparison with conversion of a blend of 20 wt% of FP oil and 80 wt% of VGO.

The results indicate that significant amounts of carbon are transferred to the gasoline, gas, LPG and coke, but less to LCO and slurry oil fraction. As a result, replacement of 20% of conventional feed by FP oil reduces the total amount of carbon fed to the FCC unit by 13% (due to the oxygen in the FP oil), but the gasoline yield dropped only by less than 5%. This might point to a synergetic effect between VGO and FP oil and the VGO seems to act as a hydrogen donor to the FP oil. Otherwise, the FP oil appears to increase the crackability of the VGO and shifts the product range towards desired light ends. In general, the co-feeding of FP oil to FCC units is not beneficial, with only an estimated 10% of the carbon from the liquids ending up in useable products (LPG and liquids). Much of the recent advances to obtain a better understanding of the co-processing of untreated FP oil in oil refineries have been conducted in BIOCOUP project within the 6th European Framework Program [39]. Particularly, various upgrading routes have been studied: (i) HDO to remove oxygen as water under high hydrogen pressure with a catalyst; (ii) high pressure thermal treatment (HPTT), in which FP oil is thermally treated to obtain an oil with a higher energy density [40]; and (iii) treatment without hydrogen, leading to decarboxylated oil (DCO). Comprehensive data on the use of FP oil either pure or as co-feed with VGO along all these routes are not published, but it is mentioned that despite lower oxygen content, a FP oil upgraded without oxygen (DCO route) could not be effectively co-processed without catalysts or hydrogen (HPTT route). An important criterion for successful co-feeding of such oils is a low-coking tendency (measured as micro carbon residue testing – MCRT), high H:C ratio, and a low average molecular weight [41].

Product yields (wt%)	VGO FCC	(20 wt% FP oil + 80 wt% VGO) FCC
Ethylene	2.0	3.3
Propylene	5.9	5.9
Propane	1.2	2.1
Butane	11.1	13.5
Gasoline	42.7	40.6
Light cycle oil (LCO)	14.8	9.1
Slurry oil	18.5	4.8
Coke	3.9	7.1
Water and CO ₂	0.0	13.4

Table 2. Product yields from co-feeding of VGO and FP oil at FCC conditions. Data from Ref. [38].

Many efforts have been made in the recent years on HDO for upgrading of FP oil to deoxygenate the organic compounds effectively into so-called HDO oils or upgraded bio-oil (UBOs). HDO of bio-oil with various catalysts (e.g. Ru/C, Ru/Al₂O₃, Ru/TiO₂, Pd/C, Pt/C, NiMo/Al₂O₃, CoMo/Al₂O₃ and Ni-based catalysts) in the past decades has been comprehensively described in reviews [42, 43]. Besides, modified strategies for HDO of bio-oil have been proposed, e.g. a mild HDO process, non-isothermal hydrotreatment, low-severity HDO [44, 45], two-stage HDO [46] and aqueous phase HDO [47].

The co-feeding of such upgraded HDO oils (20 wt%) and 80 wt% standard feedstock (Long residue) is successful in laboratory-scale even if oxygen-rich HDO oils (17–28 wt% on dry basis) are used. Product yields, e.g. for gasoline (44–46 wt%) and light cycle oil (LCO) (23–25 wt%) were retained compared to the base feed [48, 49]. The authors also carried out the co-processing of 80 wt% of SRGO + 10 wt% HDO oil + 10 wt% isopropanol (to reduce viscosity) in a lab-scale HDS reactor, but the competition between HDS and HDO was observed and the efficiency of HDS was reduced [50]. Tests on co-feeding of hydrotreated bio-oil with an aromatic hydrocarbon feedstock (15/85 wt/wt) with two commercial FCC catalysts (ReUSY1, ReUSY2) showed that the conversion was slightly lower than that of the ordinary VGO [51]. The limited crackability of the aromatic feedstock seems to be the primary reason. On the other hand, the conversion obtained from co-processing of hydrotreated bio-oil with VGO was reported to be higher than that obtained from pure VGO feed experiment [52].

Own studies on the HDO of FP oil over bimetallic catalysts (10%Ni-10%Co/HZSM-5; 300 °C and 60 bar initial H₂ pressure) resulted in an UBO, which was co-fed with conventional FCC feed (atmospheric distillation residue of Dung Quat refinery-Vietnam) in a lab-scale MAT unit [53, 54]. Several runs with the same equilibrated FCC catalyst and various fractions of UBO (10, 20, 30 wt%) in the feed and different CTO ratios were performed at FCC conditions (520 °C, 1 bar, CTO = 2.5 or 3 g/g). **Figure 2** shows that the conversion is similar for both the co-processed feeds and the 100% conventional feed, whereas a reduction of HCO yield and slight increase of gasoline, gas and LCO fraction is evident for the co-processed feeds at the CTO ratio = 3 g/g. However, at a CTO ratio of 2.5 (g/g), which correlates to somewhat milder reaction conditions in terms of residence time and respective catalyst load, the conversion decreased gradually with the increase of the UBO fraction from 80% to 65% (with the 20UBO sample). This indicates that oxygenates in the UBO are more recalcitrant to cracking due to the many O-containing functional groups and the lower H-content (e.g. phenols, guaiacols, syringols and dimers). This observation is in line with literature [44], showing that a slightly higher CTO ratio is required for co-processing of UBO with conventional feed (Long residue) in order to obtain an equivalent conversion.

The gasoline fraction is the primary objective of a FCC unit and thus its composition obtained with the 4 samples tested at a CTO ratio of 3 (g/g) was analysed and showed in **Figure 3**. Obviously, co-processed feeds give larger amounts of aromatic compounds in the gasoline as compared to 100% conventional feed. In addition, the iso-paraffin and olefin fractions were reduced compared to 100% conventional feed, while the n-paraffin and naphthene fractions were more or less of the same size.

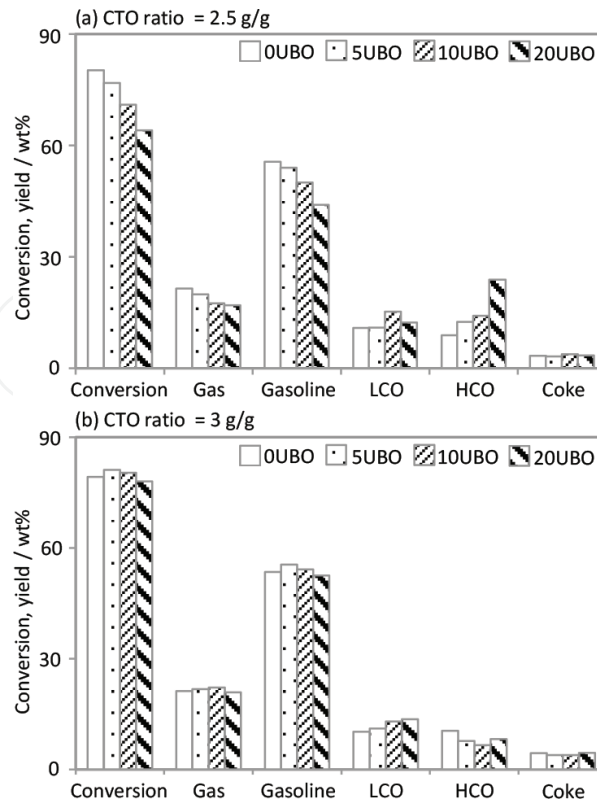


Figure 2. Performance of co-feeding tests at different feed compositions and CTO ratios in MAT unit. Adapted from Ref. [50].

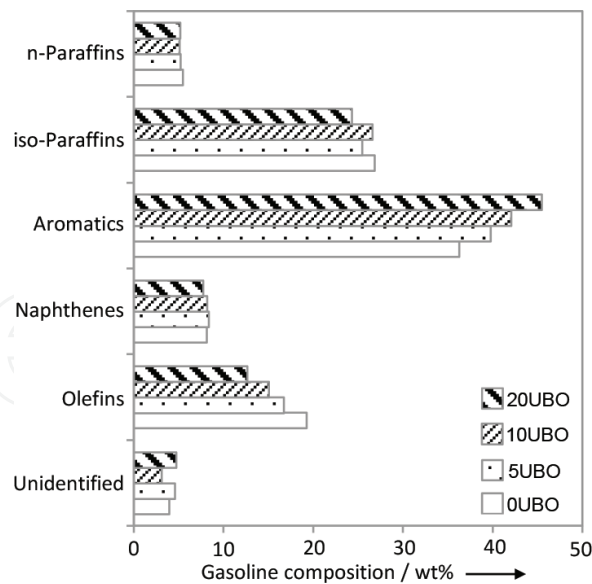


Figure 3. Gasoline composition in the products from co-feed tests at 520 °C and CTO = 3 (g/g). Adapted from Ref. [54].

On the other side, Petrobras implemented a near commercial FCC unit to co-feed pure FP oil with VGO [55]. The FP and VGO were fed into the riser reactor at two different heights. The feed rate was 150 kg/h and the results are shown in **Table 3**.

Product yields (wt%)	Feedstock		
	VGO	90% gas oil and 10% FP oil	80% gas oil and 20% FP oil
Fuel gas	3.9	2.8	2.5
LPG	15.2	12.9	9.9
Naphtha	40.4	40.7	37.7
LCO	18.1	17.4	16.5
Decanted oil	14.8	14.0	13.7
Coke	7.4	7.5	8.5
CO	0.1	1.9	3.1
CO ₂	0.1	0.5	0.8
Water	0	2.3	7.3

Table 3. Product yields from co-feeding of VGO and FP oil by Petrobras at 540 °C. Data from Ref. [55].

The results indicate that the liquid yields from the blend VGO-FP oil did not significantly drop compared to FCC of VGO, whereas the yield of fuel/LPG was dramatically decreased. The introduction of 10 wt% of FP oil did not change the gasoline yields; however, the fraction was reduced significantly when co-feeding 20 wt% of FP oil.

It can be concluded that there are substantial differences in the conversion and product patterns obtained at laboratory-scale, pilot plant and semi-commercial scale. This is understandable as different FP oil, conventional feeds and reaction conditions were used [56].

5. Summary and perspective

Co-feeding of biomass derived liquids with conventional feeds into refinery units has potential for partial replacement of fossil crudes by renewable and sustainable resources in the short-term. In addition, it might be economically advantageous for biofuels production as the capital costs could be reduced due to the use of available existing infrastructure of petroleum refineries. Various tests with both FP oil and upgraded bio-oil (UBO) not only at lab-scale, but also at the semi-demonstration FCC scale showed promising results.

Studies with phenolic model compounds provide insight into the effect of oxygenates during co-feeding on elementary steps such as hydride transfer or competitive adsorption of phenolic compounds and hydrocarbon. It seems as if hydrocarbons might act as hydrogen donor for oxygen removal from the bio-feeds. The tests with FPO or UBO indicate some crucial aspects: (i) co-feeding possibly reduces the acidity and oxygenate content in the co-feed; (ii) upgrading helps to reduce oxygen content and to increase yields of usable products (e.g. naphtha, LCO and LPG); (iii) separate injection of conventional and bio-feeds could be a suitable choice in

order to take advantage of the different reactivity of those feeds ruled by the aforementioned elementary steps.

However, the challenges of processing such bio-feeds in oil refineries are still significant and need to be further studied. As it is not expected due to economics that FCC catalyst and process design will be modified, the co-processing should be more deeply investigated using more standard conventional feeds and commercial FCC catalysts. On the other side, there might be some potential for optimisation of the upgrading step to make the UBOs more suited. As for the upstream FP process, the greater the improvement of FP, the higher the quality of bio-oil during storage and transportation and the easier the upgrading steps.

From a refiner's perspective, the important properties are the boiling-range distribution and the acidity. The high oxygen content of FP oil and UBO might cause corrosion and augmented coking of catalyst surfaces as well as downstream contamination risks. Thus, the upgrading of bio-feed to what extent should be adapted to the requirement of the refinery. It is likely that the degree of deoxygenation correlates with the oil yield and the heating value of UBO. Besides, another issue is to identify the best inlets for bio-feeds into the refinery and the requirements for venting of oxygenated gases (e.g. CO and CO₂) should be considered as it is not usual in conventional refinery.

Finally, one question might be open for the reader: who will responsible for the control and the management of bio-feeds and their co-processing into refinery? A realistic scenario will be that both industries cooperate, one producing the biofuel precursors and the other processing and converting them into valuable fuels.

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References

- [1] BP Statistical Review of World Energy. 2015; Available from: www.bp.com/en/global/corporate/about-bp/energy-economics/statistical-review-of-world-energy.html [Accessed: 2015-06-20].
- [2] Wang H, Male J, Wang Y. Recent advances in hydrotreating of pyrolysis bio-oil and its oxygen-containing model compounds. *ACS Catalysis*. 2013; **3**: 1047–1070.

- [3] Kuparinen K, Heinimö J, Vakkilainen E. World's largest biofuel and pellet plants- geographic distribution, capacity share, and feedstock supply. *Biofuels Bioproducts and Biorefining*. 2014; **8**: 747–754.
- [4] Carpenter D, Westover TL, Czernik S, Jablonski W. Biomass feedstocks for renewable fuel production: a review of the impacts of feedstock and pretreatment on the yield and product distribution of fast pyrolysis bio-oils and vapors. *Green Chemistry*. 2014; **16**: 384–406.
- [5] Saxena RC, Adhikari DK, Goyal HB. Biomass-based energy fuel through biochemical routes: a review. *Renewable Sustainable Energy Review*. 2009; **13**: 167–178.
- [6] Regalbuto JR. Cellulosic biofuels – got gasoline?. *Science*, 2009; **325**: 822–824.
- [7] Huber GW, Corma A. Synergies between bio- and oil refineries for the production of fuels from biomass. *Angewandte Chemistry International Edition*. 2007; **46**: 7184–7201.
- [8] Saidi M, Samimi F, Karimipourfard D, Nimmanwudipong T, Gates BC, Rahimpour MR. Upgrading of lignin-derived bio-oils by catalytic hydrodeoxygenation. *Energy and Environmental Science*. 2014; **7**: 103–129.
- [9] Talmadge MS, Baldwin RM, Biddy MJ, McCormick RL, Beckham GT, Ferguson GA, Czernik S, Magrini-Bair KA, Foust TD, Metelski PD, Hetrick C, and Nimlos MR, A perspective on oxygenated species in the refinery integration of pyrolysis oil. *Green Chemistry*. 2014; **16**: 407–453.
- [10] Wauquier JP. *Petroleum Refining. Vol. 1 Crude Oil. Petroleum Products. Process Flowsheets*, IFP, Paris, 1995, ISBN: 9782710806851.
- [11] Huber GW, Iborra S, Corma A. Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. *Chemical Reviews*. 2006; **106**: 4044–4098.
- [12] Elliott DC. Historical developments in hydroprocessing bio-oils. *Energy Fuels*. 2007; **21**: 1792–1815.
- [13] Zacher AH, Olarte MV, Santosa DM, Elliott DC, Jones SB. A review and perspective of recent bio-oil hydrotreating research. *Green Chemistry*. 2014; **16**: 491–515.
- [14] Mortensen PM, Grunwaldt JD, Jensen PA, Knudsen KG, Jensen AD. A review of catalytic upgrading of bio-oil to engine fuels. *Applied Catalysis A: General*. 2011; **407**: 1–19.
- [15] He Z, Wang X. Hydrodeoxygenation of model compounds and catalytic systems for pyrolysis bio-oils upgrading. *Catalysis for Sustainable Energy*. 2013; **1**: 28–52 (DOI: 10.2478/cse-2012-0004).
- [16] Ruddy DA, Schaidle JA, Ferrell JR, Wang J, Moens L, Hensley JE. Recent advances in heterogeneous catalysts for bio-oil upgrading via “ex situ catalytic fast pyrolysis”: catalyst development through the study of model compounds. *Green Chemistry*. 2014; **16**: 454–490.
- [17] Huynh TM, Armbruster U, Martin A. Deoxygenation of Liquefied Biomass. In: Cavani F, Albonetti S, Basile F, Gandini A, editors. *Chemicals and Fuels from Bio-Based Building Blocks*. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2016, pp. 403–430.

- [18] Melero JA, Iglesias J, Garcia A. Biomass as renewable feedstock in standard refinery units. Feasibility, opportunities and challenges. *Energy and Environmental Science*. 2012; **5**: 7393–7420.
- [19] Bu Q, Lei H, Zacher AH, Wang L, Ren S, Liang J, Wei Y, Liu Y, Tang J, Zhang Q, Ruan R. A review of catalytic hydrodeoxygenation of lignin-derived phenols from biomass pyrolysis. *Bioresource Technology*. 2012; **124**: 470–477.
- [20] Huynh TM, Armbruster U, Pohl MM, Schneider M, Radnik J, Hoang DL, Phan BMQ, Nguyen DA, Martin A. Hydrodeoxygenation of phenol as a model compound for bio-oil on non-noble bimetallic nickel-based catalysts. *ChemCatChem*. 2014; **6**: 1940–1951.
- [21] Huynh TM, Armbruster U, Phan BMQ, Nguyen DA, Martin A. The influence of cobalt in bimetallic Ni-Co catalyst supported on H-Beta for phenol hydrodeoxygenation. *Chimica Oggi-Chemistry Today*. 2014; **32**: 40–44.
- [22] Bykova MV, Ermakov DY, Kaichev VV, Bulavchenko OA, Saraev AA, Lebedev MY, Yakovlev VA. Ni-based sol-gel catalysts as promising systems for crude bio-oil upgrading: guaiacol hydrodeoxygenation study. *Applied Catalysis B: Environmental*. 2012; **113–114**: 296–307.
- [23] Sun J, Karim AM, Zhang H, Kovarik L, Li XS, Hensley AJ, McEwen JS, Wang Y. Carbon-supported bimetallic Pd-Fe catalysts for vapor-phase hydrodeoxygenation of guaiacol. *Journal of Catalysis*. 2013; **306**: 47–57.
- [24] Zhao C, Lercher JA. Upgrading pyrolysis oil over Ni/HZSM-5 by cascade reactions. *Angewandte Chemistry International Edition*. 2012; **51**: 1–7.
- [25] Zhao C, Lercher JA. Selective hydrodeoxygenation of lignin-derived phenolic monomers and dimers to cycloalkanes on Pd/C and HZSM-5 catalysts. *ChemCatChem*. 2012; **4**: 64–68.
- [26] Bui VN, Toussaint G, Laurenti D, Mirodatos C, Geantet C. Co-processing of pyrolysis bio-oils and gas oil for new generation of bio-fuels: hydrodeoxygenation of guaiacol and SRGO mixed feed. *Catalysis Today*. 2009; **143**: 172–178.
- [27] Senol O, Ryymin EM, Viljava TR, Krause AOI. Effect of hydrogen sulphide on the hydrodeoxygenation of aromatic and aliphatic oxygenates on sulphided catalysts. *Journal of Molecular Catalysis A: Chemical*. 2007; **277**: 107–112.
- [28] Laurent E, Delmon B. Influence of water in the deactivation of a sulfide NiMo/Al₂O₃ catalyst during hydrodeoxygenation. *Journal of Catalysis*. Illinois, 1994; **146**: 281–285.
- [29] Corma A, Huber GW, Sauvinaud L, O'Connor P. Processing biomass-derived oxygenates in the oil refinery: catalytic cracking (FCC) reaction pathways and role of catalyst. *Journal of Catalysis*. 2007; **247**: 307–327.
- [30] Domine ME, van Veen AC, Schuurman Y, Mirodatos C. Coprocessing of oxygenated biomass compounds and hydrocarbons for the production of sustainable fuel. *ChemSusChem*. 2008; **1**: 179–181.

- [31] Graça I, Ribeiro FR, Cerqueira HS, Lam YL, de Almeida MBB. Catalytic cracking of mixtures of model bio-oil compounds and gasoil. *Applied Catalysis B: Environment*. 2009; **90**: 556–563.
- [32] Graça I, Lopes JM, Ribeiro MF, Ribeiro FR, Cerqueira HS, de Almeida MBB. Catalytic cracking in the presence of guaiacol. *Applied Catalysis B: Environment*. 2011; **101**: 613–621.
- [33] To AT, Resasco DE. Hydride transfer between a phenolic surface pool and reactant paraffins in the catalytic cracking of m-cresol/hexanes mixtures over an HY zeolite. *Journal of Catalysis*. 2015; **329**: 57–68.
- [34] Vispute TP, Huber GW. Production of hydrogen, alkanes and polyols by aqueous phase processing of wood-derived pyrolysis oils. *Green Chemistry*. 2009; **11**: 1433–1445.
- [35] Adjaye JD, Bakhshi NN. Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. *Fuel Processing Technology*. 1995; **45**: 185–202.
- [36] Vitolo S, Bresci B, Seggiani M, Gallo MG. Catalytic upgrading of pyrolytic oils over HZSM-5 zeolite: behaviour of the catalyst when used in repeated upgrading–regenerating cycles. *Fuel*. 2001; **80**: 17–26.
- [37] Al-Sabawa M, Chen J, Ng S. Fluid catalytic cracking of biomass-derived oils and their blends with petroleum feedstocks: a review. *Energy Fuels*. 2012; **26**: 5355–5372.
- [38] Marinangeli R, Marker T, Petri J, Kalnes T, McCall M, Mackowiac D, Jerosky B, Regan B, Nemeth L, Krawczyk M, Czernik S, Elliott D, Shonnard D. 2006. Opportunities for Biorenewables in Oil Refineries, UOP, Report No. DE-FG36-o5GO15085.
- [39] <http://www.biocoup.com/> [Accessed: 2016-09-09].
- [40] de Miguel Mercader F, Groeneveld MJ, Kersten SRA., Venderbosch RH, Hogendoorn JA. Pyrolysis oil upgrading by high pressure thermal treatment. *Fuel*. 2010; **89**: 2829–2837.
- [41] Karatzos S, McMillan JD, Saddler JN. 2014. The potential and Challenges of Drop-in fuels, IEA Bioenergy Task 39, Available from: <http://task39.org/2014/01/the-potential-and-challenges-of-drop-in-fuels-members-only/> [Accessed: 2016-09-20].
- [42] Elliott DC, Biller P, Ross AB, Schmidt AJ, Jones SB. Hydrothermal liquefaction of biomass: developments from batch to continuous process. *Bioresource Technology*. 2015; **178**: 147–156.
- [43] Choudhary TV, Phillips CB, Renewable fuels via catalytic hydrodeoxygenation. *Applied Catalysis A: General*. 2011; **397**: 1–12.
- [44] Elliott DC, Baker EG, Piskorz J, Scott DS, Solantausta Y. Production of liquid hydrocarbon fuels from peat. *Energy Fuels*. 1988; **2**: 234–235.
- [45] Baldauf W, Balfanz U, Rupp M. Upgrading of flash pyrolysis oil and utilization in refineries. *Biomass Bioenergy*. 1994; **7**: 237–244.
- [46] French RJ, Stunkel J, Baldwin RM. Mild hydrotreating of bio-oil: effect of reaction severity and fate of oxygenated species. *Energy Fuels*. 2011; **25**: 3266–3274.

- [47] Vispute TP, Zhang H, Sanna A, Xiao R, Huber GW. Renewable chemical commodity feedstocks from integrated catalytic processing of pyrolysis oils. *Science*. 2010; **330**: 1222–1227.
- [48] de Miguel Mercader F, Groeneveld MJ, Kersten SRA, Way NWJ, Schaverien CJ, Hogendoorn JA. Production of advanced biofuels: co-processing of upgraded pyrolysis oil in standard refinery units. *Applied Catalysis B: Environmental*. 2010; **96**: 57–66.
- [49] de Miguel Mercader F, Groeneveld MJ, Kersten SRA, Geantet C, Toussaint G, Way NWJ, Schaverien CJ, Hogendoorn KJA. Hydrodeoxygenation of pyrolysis oil fractions: process understanding and quality assessment through co-processing in refinery units. *Energy and Environmental Science*. 2011; **4**: 985–997.
- [50] de Miguel Mercader F, Koehorst PJJ. Competition between hydrotreating and polymerization reactions during pyrolysis oil hydrodeoxygenation. *AIChE Journal*. 2011; **57**: 3160–3170.
- [51] Samolada MC, Baldauf W, Vasalos IA. Production of a bio-gasoline by upgrading biomass flash pyrolysis liquids via hydrogen processing and catalytic cracking. *Fuel*. 1998; **77**: 1667–1675.
- [52] Fogassy G, Thegarid N, Toussaint G, van Veen AC, Schuurman Y, Mirodatos C. Biomass derived feedstock co-processing with vacuum gas oil for second-generation fuel production in FCC units. *Applied Catalysis B: Environmental*. 2010; **96**: 476–485.
- [53] Huynh TM, Armbruster U, Nguyen LH, Nguyen DA, Martin A. Hydrodeoxygenation of bio-oil on bimetallic catalysts: from model compound to real feed. *Journal of Sustainable Bioenergy Systems*. 2015; **5**: 151–160.
- [54] Huynh TM, Armbruster U, Atia H, Bentrup U, Phan BMQ, Eckelt R, Nguyen LH, Nguyen DA, Martin A. Upgrading of bio-oil and subsequent co-processing under FCC conditions for fuel production. *Reaction Chemistry & Engineering*. 2016; **1**: 239–251.
- [55] Pinho AR, de Almeida MBB, Mendes FL, Ximenes VL, Casavechia LC. Co-processing raw bio-oil and gasoil in an FCC Unit. *Fuel Processing Technology*. 2015; **131**: 159–166.
- [56] Al-Sabawi M, Chen J, Ng S. Fluid catalytic cracking of biomass-derived oils and their blends with petroleum feedstocks: a review. *Energy Fuels*. 2012; **26**: 5355–5372.

