Mini-review

Perspective on biomass derived bio-oil valorization in Viet Nam

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Abstract

Various strategies for biomass derived bio-oil valorization as a renewable feedstock for chemicals and fuels are described. Starting from the role of renewable resources (e.g. biomass, bio-oil) in the future energy and chemical community, an overview on current energy supply situation and the role of biomass and related products are discussed. Later, summary of bio-oil production from biomass and the need for upgrading to further uses is represented. Subsequently, the valorization of bio-oil as fuels and feedstocks are intensively summarized, showing the potential utilization of bio-oils via such processes. Some studies on biomass assessment, bio-oil production and upgrading in Vietnam are also given. Finally, some concluding remarks address the perspectives for further research and development to overcome future challenges.

Keywords. Bio-oil valorization, bio-oil/diesel emulsion, co-feeding, deoxygenation, refinery units.

1. INTRODUCTION

The basement of the presently consumed energy is significantly depending on the fossil fuels (e.g. crude oil, coal and natural gas). According to British Petroleum statistical review of world energy 86 % and 81 % of primary energy in the US and Germany in 2014 are from those sources, respectively [1]. A minor portion is come from other resources (e.g. biomass, nuclear and hydroelectric power, wind, solar, and geothermal) [1]. In order to cope with the increasing of energy demand, the growing environmental concerns and the limited availability of fossil fuels reserves, the search for renewable and sustainable resources is needed to serve as alternatives to close future gaps in term of transportation fuels supply as well as of feedstock for chemical industry. Moving the world market dependence away from fossil-based resources to renewable ones will definitely contribute to the climate protection and sustainable economy.

Hence, many researchers have recently turned attention to biomass resources due to several reasons. First, biomass production is only carbon-based feed and based on short-time carbon cycles and overall CO_2 neutral. Second, biomass is a cheap, abundant and sustainable raw material. Additionally, some types of biomass like vegetable oils already fit quite well into the present carbon-based fuel infrastructure [1-3].

As a result, the governments of many countries have set ambitious goals and 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. As a developing country, Vietnam also involves in the biomass based energy due to a generated huge amount of agricultural residues (approximately 62 million tons per year) [2].

However, 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 product (so called bio-oil) is necessary as a primary step. Fast pyrolysis (FP) or hydrothermal liquefaction (LF) seems to be potential technologies for liquefying biomass [2, 3]. Usually, such obtained bio-oil can be used as a direct fuel oil for power generation commercially. However, they are really difficult to use directly as a transportation fuel due to their oxygen contents varying in a range of 35-45 wt%, which has to be lowered prior to any use. Additionally, undesired properties like low specific energy content will be serious drawbacks for application as fuels compared to conventional fuels [2, 3]. Other valorization methods such as solvent addition/esterification or emulsification with conventional fuels oil (e.g. diesel oil) have been studied and evaluated in order to produce a

emulsified/blended oil for drop-in fuels or chemical feedstocks.

The following paragraphs might give the main aspects involved in various utilization of bio-oil as a fuels oil, blended fuels, petrochemical and refinery units feedstock. A summary of FP of biomass and bio-oil upgrading studies in Vietnam are also discussed. A perspective on research and development is ultimately given in order to cope with the future challenge.

2. OVERVIEW OF BIOMASS RESOURCES AND BIO-OIL PRODUCTION

2.1. Biomass Resources Overview

Current production of first-generation biofuels (e.g. bioethanol and biodiesel) and blending in conventional fuels (gasoline, diesel) up to 10 vol% are steps in the right direction. However, the use of first generation biomass feedstocks (e.g. starch, sugar, animal fats, and vegetable oil) are limited and might compete with the nutrition demand, affecting feeds availability and prices. Additionally, they need fertile land and water and might partly destroy nature and environment. The access to renewable biofuels from biomass resources offered by agriculture, forestry, and industry have great potential for fuels and chemicals production [2]. The second generation biomass is referred to the ligno-cellulosic biomass and includes a variety of materials such as agricultural residues, woods and lignin residues, which are available around the world. Cellulose, hemicellulose and lignin are three main components of such raw materials in portions of approximately 35-45 %, 25-35 % and 15-25 %, respectively. Therefore, these materials possess oxygen contents varying in a range of 35-45 wt%, which is far different from conventional fossil feeds. Besides that, biomass has low volumetric and energy densities, resulting in high cost for collecting and transportation. As a result, converting biomass to liquid form seems to be a good option dealing with these characteristics.

Our survey on biomass resources showed that agricultural residues in Vietnam (e.g. rice straw, rice husk, corncob, bagasse) are abundant (approximately 62 million tons annually), but these residues are not effectively used. Usually, they are burned or disposed to the environment, whereas the rest are used for making pellest or for local electricity generation [2]. Thus, biomass resouces could be potential renewable feedstocks for fuels and petrochemicals.

2.2 Bio-oil Production from Biomass

Regarding the technology platforms, there are several general pathways for transformation of biomass to liquid fuels that can be simply separated based on primary processes such as hydrolysis-fermentation (biochemical route), gasification and FP/LF (thermal-chemical routes) [9]. In the latter case, biomass can be converted to mainly liquid oil (so called bio-oil) in the absence of oxygen. FP is fundamentally the thermal decomposition process in which biomass is rapidly heated in a typical temperature range (450-550 °C) with very short residence time (1-2 s) at atmospheric pressure or lower [8]. On the other side, LF is carried out in mostly hot liquid water with or without catalysts under lower temperature (300-400 °C), but higher pressure (120-200 bar) compared to FP technology [2, 3]. One of the advantages of LF is the direct processing of wet biomass without pre-drying; however, the process operates under high pressure which results in some technical difficulties and an increase of capital cost. FP technology appeared as a promising method which has been first developed in the later 1970s. Several aspects of this technology have been studied. In fact, four main reactor technologies have been developed and are currently available for commercialization, including fluidized bed (Dynamotive - 8,000 kg/h), circulating fluidized bed (Ensyn - 4,000 kg/h), rotating cone (BTG-2,000 kg/h), ablative pyrolyser (PYTEC-250 kg/h). A state of the art for FP technology has been reviewed in detail elsewhere [2]. Our group at Vietnam Petroleum Institute (VPI) conducted the bio-oil production from Vietnamese biomass via lab-scale FP technology (fluided bed reactor) and the result revealed that the obtained bio-oil fulfilled the specifications for pyrolysis liquid defined in ASTM D7544-12 [6]. The second phase of this project is being carried out on a fast pyrolysis pilot at VPI with a capacity of 5 kg/h in order to evaluate more detail in technical and economic aspects which will be sum up at the end of this year.

Figure 1 illustrates the structure of the three main components of biomass and variety of common detected monomer oxygenates with various functional groups (e.g. acids, alcohols, phenols, sugars, aldehydes, ketones and esters etc.) in bio-oil [7]. Additionally, phenolic dimers are detected largely in bio-oil, especially in lignin derived bio-oil. Remarkably, more than 200 oxygenate compounds in bio-oils are known, having various types of functional groups with specific chemistry. The high oxygenates content in bio-oil causes some negative characteristics such as low volatility, high viscosity,

immiscibility with conventional fuels, and instability during long-time storage. Normally, bio-oil reveals a general sum formula of $CH_{1.4}O_{0.4}$, whereas conventional liquid fuel or hydrocarbons show a sum formula close to CH_2 and thus, its quality is far away from conventional liquid fuels. It is necessary

therefore to further reduce the oxygen content to improve the quality via upgrading and ultimately make it suitable for further uses as a chemical feedstock or a fuel component. In the next section, biomass valorization is further discussed.
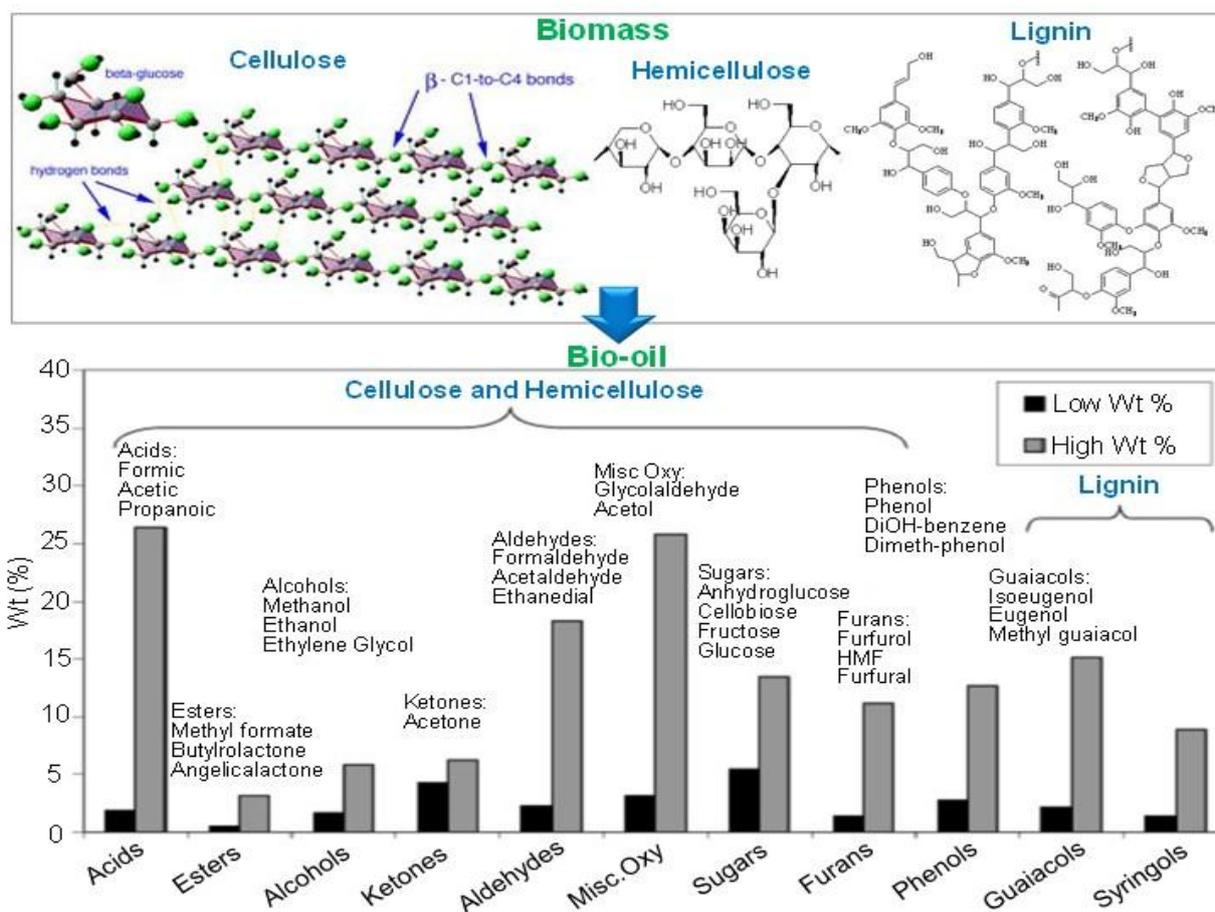

Figure 1: Main components of biomass and typical chemical composition of bio-oil. Adapted from [7]

3. BIO-OIL VALORIZATION

3.1. Bio-oil as a Feedstock for Fuels and Chemicals

As a renewable liquid fuel, bio-oil can be readily stored and transported. It can serve as a substitute for fuel oil in boiler, furnaces and turbines for heat generation [2, 3] and for diesel engines/turbines for power applications [2].

As stated above, upgrading of bio-oil is necessary for further use as a drop-in fuel because of high oxygenate and water content. There are several pathways that have been proposed for partial or total bio-oil deoxygenation such as hydrotreating or hydrodeoxygenation (HDO), catalytic cracking, aqueous phase reforming, steam reforming,

esterification, gasification etc. (e.g. [2, 3]). Among the available upgrading strategies, HDO supported by catalysts is considered as most effective technology for deep deoxygenation [2, 3]. Various supported metal catalysts (e.g. Pd/C, Pt/C, Ru/C, Ru/Al_2O_3, Ru/TiO_2) and conventional hydrotreating catalysts ($NiMo/Al_2O_3$, $CoMo/Al_2O_3$) were intensively evaluated for HDO of bio-oil, e.g. by Wildschut et al. [2]. We also developed the catalysts for HDO based on monometallic and bimetallic Ni based catalysts (Ni, Ni-Co, Ni-Cu) supported on different acidic supports (H-ZSM-5, H-Beta, H-Y, and ZrO_2). The studies on HDO of phenol and intermediates on at mild conditions (250 °C, 50 bar initial H_2 pressure) [2, 3] and then applied those catalysts for real bio-oil HDO [2] were successful and the Ni-Co/HZSM-5 showed the best performing

catalyst owing to the formation of Ni-Co alloy with small particle size and instrinsic properties in the catalyst [24]. Several aspects for upgrading technology strategies and catalyst development for deep oxygenate reduction have been achieved in the last decade. However, the total removal of oxygenates from bio-oil for direct use in transportation fuels is very challenging. Severe reaction conditions (high temperature and pressure) and high energy input (hydrogen consumption) are required to achieve high degree of deoxygenation and complete conversion. A detailed review on the deoxygenation of bio-oil and related model compounds in standalone units have been reported in our book chapter [2].

Another strategy has been proposed for bio-oil quality improvement. The use of catalysts for the up-stream FP process have been studied via in-situ or online-upgrading of vapour bio-oil in order to provide a suitable bio-oil for further processing (e.g feedstock for chemicals, fuels). In this aspect, we performed the online upgrading of vapour from FP of Vietnamese biomass [28]. The result revealed that sodium carbonate supported on γ-alumina and HZSM-5 catalysts are shown to possess excellent activity in the bio-oil deoxygenation in opposite ways. $Na_2CO_3/\gamma-Al_2O_3$ materials was shown to be efficient in the deoxygenation of alkoxy phenols into phenol while HZSM-5 favours in the oxygen removal of oxygenates into aromatic hydrocarbons. These findings might provide a suitable strategy to catalytically upgrade bio-oil depending on its applications as fuel or petrochemical feedstock.

Alternatively, different specialty chemicals form the bio-oils are also possible after further processing, extraction and separation and could serve as a raw material for the production of adhesives, phenol-formaldehyde-type resins, wood flavors, etc. For example, production of levoglucosan based feed, which has potential in the manufacturing of pharmaceuticals, surfactants, biodegradable polymers [2]. Bio-oil can be used as liquid smoke and wood flavors [2] and production of chemicals and resins (e.g. demission control agents) [2, 3] and in making adhesives [2].

3.2. Bio-oil as a Co-feed in Standard Refinery Units

To increase the renewable fuel capacity, co-processing with conventional feed in current refinery infrastructure seems to be an attractive option in the mid-term as the capital and operational costs would be marginal.

As mentioned above, bio-oils obtained from FP or LF of 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 [2]. Conversion of pure bio-oil from FP technology over conventional fluid catalytic cracking (FCC) catalysts has been studied in the nineties [2, 3]. However, a certain problems were observed such as nozzle plugging, irreversible catalyst deactivation owing to significant formation of coke, tar, and char, causing a more severe catalyst deactivation [2]. 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 bio-oil with conventional feed before feeding into refinery unit is the logical alternative owing to the interest of petroleum oil companies.

Micro Activity Test (MAT) or Advanced Cracking Evaluation (ACE) are the standard lab-scale techniques for evaluation of FCC catalysts and might also simulate the co-processing of bio-oil with conventional FCC feeds. Such tests are known to elucidate the actual behaviour of commercial FCC units quite well, and various parameters (e.g. temperature, catalyst to oil (CTO) ratios) can be systematically investigated to check the difference from conversion, products distribution and compositions. For example, UOP reported the first results for such processing tests in an ACE test unit [2]. Table 1 provides typical results for VGO cracking compared with conversion of a blend of 20 wt% of bio-oil and 80 wt% of VGO.

Table 1: Product yields from co-processing of VGO and bio-oil at FCC conditions. Data from [38]

Product yields, wt%	VGO	(20 wt% Bio-oil + 80 wt% VGO)
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

The results reveal that significant amounts of carbon from bio-oil are transferred to the gasoline, gas, LPG, and coke but less to LCO and slurry oil fractions. As a result, replacement of 20 % of

conventional feed by bio-oil reduces the total amount of carbon fed to the FCC unit by 13% (due to the oxygen in the bio-oil), but the gasoline yield dropped only by less than 5 %. This can be attributed to a synergetic effect between VGO and bio-oil, and the VGO seems to act as a hydrogen donor to the bio-oil. Otherwise, the bio-oil appears to increase the crackability of the VGO and shifts the product range towards desired light ends. In general, the co-processing of untreated bio-oil to FCC units is not beneficial because of only an estimated 10 % of the carbon from the liquids ending up in useable products (LPG and liquids). Much of the recent advances have been conducted in BIOCOUP project within the 6th European Framework Program to obtain a better understanding of the co-processing of untreated bio-oil into standard refinery units [2]. Comprehensive data on either pure bio-oil use or as co-feed with VGO are not published, but it is indicated that despite lower oxygen content, a bio-oil upgraded without hydrogen (decarboxylated oil route) and without catalysts (high pressure thermal treatment route) could not be effectively co-processed. Low-coking tendency, high H/C ratio, and a low average molecular weight of the upgraded bio-oil are important criterion for successful co-feeding [2].

Many efforts have been made in the recent years on HDO for bio-oil upgrading and catalyst development in order to deoxygenate the organic compounds effectively into so-called HDO oils or upgraded bio-oil (UBO). HDO of bio-oil with various catalysts in the past decades has been comprehensively described in reviews [2, 3]. Besides, modified strategies for bio-oil HDO have been proposed, e.g., a mild HDO process, non-isothermal, low-severity HDO [2, 3], aqueous phase HDO [2], two-stage HDO [2].

The co-feeding of such UBO 20 wt% and 80 wt% standard feedstock (Long residue) is successful in lab-scale even if oxygen-rich UBO (17-28 wt% on dry basis) are used. Product yields, e.g. for gasoline (44-46 wt.%) and LCO (23-25 wt.%) were retained compared to the base feed [2, 3]. The authors also tested on co-processing of 80 wt% of SRGO+10 wt% UBO+10 wt% isopropanol (to reduce viscosity) in a lab-scale hydrodesulfurisation (HDS) reactor, but competition between HDS and HDO was observed and thus the efficiency of HDS was reduced [2]. Another report by Fogassy et al. [2] revealed that the conversion obtained from co-processing of UBO with VGO was reported to be higher than that obtained from pure VGO feed.

Our studies on the HDO of bio-oil over bimetallic catalysts (10%Ni-10%Co/HZSM-5, 300

°C, 60 bar initial H_2 pressure) and subsequent co-fed with conventional FCC feed (atmospheric distillation residue of Dung Quat refinery-Vietnam) in a lab-scale MAT unit was successful [2, 26, 52]. Several tests with the same equilibrated FCC catalyst and various fractions of UBO (5, 10, 20 wt%) in the feed and different CTO ratios were performed at FCC conditions (520 °C, 1 bar, CTO = 2.5 or 3 g/g). The result in 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 catalyst load and residence time, 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).
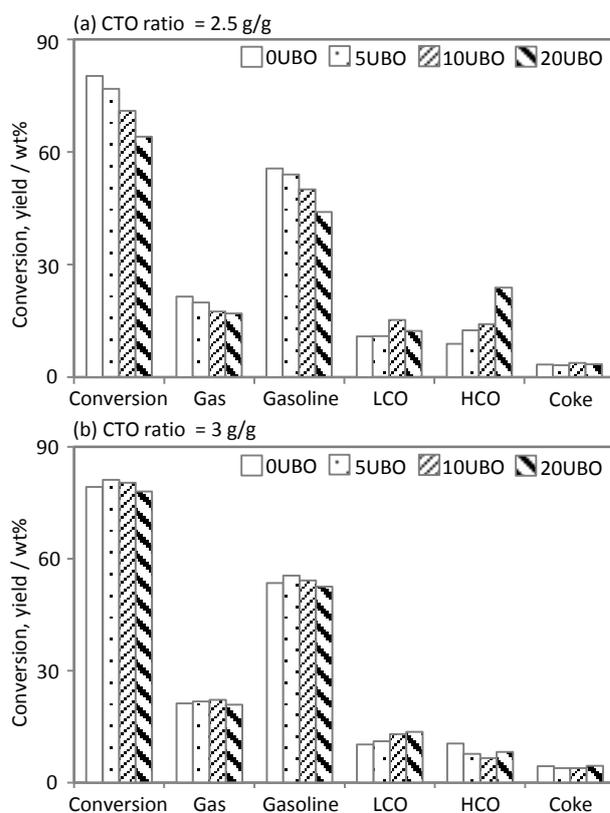

Figure 2: Performance of co-feeding tests at different feed compositions and CTO ratios in MAT unit. Adapted from [51]

Figure 3 depicts the gasoline composition obtained with the four samples tested at a CTO ratio

of 3 (g/g). Obviously, co-processed feeds give larger amounts of aromatic compounds in the gasoline as compared to 100 % conventional feed. In addition, the olefins and iso-paraffin fractions were reduced compared to 100 % conventional feed while the n-paraffin and naphthene fractions were more or less of the same size.
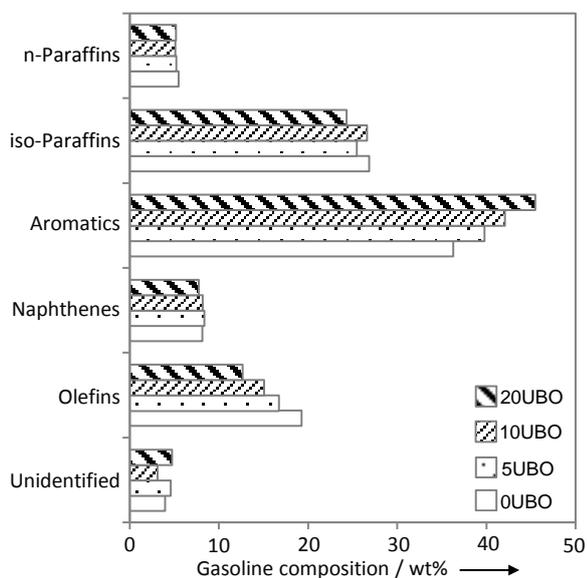

Figure 3: Gasoline composition in the products from MAT tests at 520 °C and CTO = 3 (g/g). Adapted from [51]

It is likely that the degree of deoxygenation correlates with the oil yield and the heating value of UBO. Thus, the upgrading of bio-oil to what extent should be adapted to the requirement of the refinery. More information about the co-feeding of bio-oil/UBO into refinery units, please refer to our book chapter [2].

3.3. Bio-oil as a Co-feed in Diesel Emulsion Fuels

One of the methods of bio-oil valorization is produce an emulsion with other fuel sources (e.g. diesel oil) and used as a combustion fuel in diesel engines or boilers. Bio-oils are not miscible with hydrocarbon fuels, but with the aid of surfactants they can be emulsified with diesel oil. Upgrading of bio-oil through emulsification with diesel oil has been investigated by many researchers [2-4]. A process for producing stable micro emulsions, with 5-30 % of bio-oil in diesel has been developed at Canmet Energy Technology Centre [2]. Those emulsion fuels are less corrosive and show promising ignition characteristics.

Chiaramonti et al. [56] tested the emulsions from bio-oil and diesel in engines, suggesting that

corrosion accelerated by the high velocity turbulent flow in the spray channels is the dominant problem. A stainless steel nozzle has been built and successfully tested. Long-term validation however, is still needed.

Our own study also focused on emulsified fuels including diesel oil (80 %), bio-oil (5-10 %), and surfactant (10-15 %). The obtained fuel really stable after 72 h on during storage and can be used for small engines. The fuel consumption for both pure diesel oil and emulsified fuel are more or less the same, whereas the generated emission is not significantly different.

Overall, bio-oil utilization through emulsification with diesel oil is relatively simple and it can be seen as a short-term approach. The emulsions showed promising ignition characteristics, but fuel properties such as heating value, cetane and corrosivity were still unsatisfied. Additionally, this process required high energy for production. Futher requirement for design, production and testing of injectors and fuel pumps made from stainless steel or other materials is needed.

4. SUMMARY AND PERSPECTIVE

Bio-oil from waste biomass has great potential for a feedstock to renewable fuels and chemicals and feedstocks. It can be used as substitute for fuel oil for heat and power generation. However, the direct use is mostly impossible because of the immiscibility with conventional fuels, the high oxygen content and the considerable amount of water and thus post-treatment by deoxygenation is necessary.

Upgrading of bio-oil can be done via post-treatment or up-stream processes. The greater the improvement of FP, the higher the quality of bio-oil and the easier the upgrading steps and subsequent the utilization. Catalytic fast pyrolysis seems to be an potential strategy for different application depending on specific catalysts. In the future, it should be concentrated on suitable catalyst with high performance and long life. Valorization of bio-oil can be done in various methods and depend on the final application. Up to now, the deep deoxygenation of bio-oil into drop-in fuels (gasoline, diesel) requires high energy input and severe reaction conditions. The development of more suitable catalysts should be continued in order to improve the catalyst performance and avoid the metal agglomeration during reaction. Trials with Ni-Co alloys on micro-mesoporous composites material might improve the hydrothermal stability and accessibility.

Co-feeding of bio-oil with conventional feeds into refinery units (e.g. FCC) has potential for partial replacement of fossil feeds by renewable and sustainable resources in the short-term. It not only takes the advantage of the mature technologies but also reduces the capital costs due to the use of available existing infrastructure of petroleum refineries. Various tests with both conventional feeds and upgraded bio-oil (UBO) at lab-scale and semi-demonstration FCC scale showed promising results. From a refiner's perspective, boiling-range distribution and the acidity are the important properties. The high oxygen content of bio-oil and UBO might cause augmented catalyst surface coking, corrosion as well as downstream contamination risks. Thus, the upgrading of bio-oil to what extent should be adapted to the requirement of the refinery. Another issue is to identify the best inlets for bio-oil into the refinery. Separate injection of conventional and bio-oils could be a suitable choice in order to take advantage of the different reactivity of those feeds. The requirements for venting of oxygenated gases (e.g. CO, CO_2) should be considered as it is not usual in conventional refinery.

Development of bio-oil diesel emulsion fuels is also a short-term approach. Further studies should be focused on finding out the high-efficient surfactants.

Finally, one question might be open for the reader: who will responsible for the control and the management of bio-oil in current and future refinery and chemical community?

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