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Refinery co-processing of renewable feeds

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ABSTRACT

Biofuels are called upon to play an important role, not only in reducing the associated greenhouse-gases emissions, but also in enabling the gradual independence from fossil sources, rendering low-carbon-highly-sustainable fuels. Today, the involvement of biomass-derived sources into existing petroleum refineries has a growing interest due to the increasing unpredictability of oil prices, environmental concerns and the necessity to secure an energy supply. Petroleum refineries already have a well-developed infrastructure to produce fuels and base chemicals and, consequently, would not require additional intensive investments for processing of alternative feedstocks. From this point of view, co-processing of biomass-derived feedstocks with petroleum fractions is an attractive option, which has already been industrially demonstrated in some cases. There are two main technologies that could be used for co-processing of biomass feedstocks with petroleum fractions, the first one being catalytic hydroprocessing and the second one being fluid catalytic cracking (FCC). Both technologies are found in virtually any conventional refinery. It is obvious that the co-processing of biomass-based feedstocks with petroleum fractions has the potential to play an important role in the near future. There are several research studies in literature that examine both technologies for co-processing. However, while there are many technological reviews that focus on stand-alone biofuel production (*e.g.*, FAME biodiesel, bioethanol, HVO *etc.*), a dedicated technological review on co-processing for production of hybrid fuels is still missing. Therefore, this paper is focused on presenting a state-of-the-art review on co-processing bio-based feedstocks with petroleum fractions via hydroprocessing and fluid catalytic cracking, looking at different potential feedstocks, catalysts, operating conditions, products and benefits in detail. As there is no specifically dedicated literature review in this field, the content of this review provides a guideline on co-processing of different bio-based feedstocks with petroleum fractions, aimed at delivering a technological assessment of the existing research efforts.

Contents

Abbreviations: ACE-R™, Advanced Cracking Evaluation; ACE™, Advanced Catalyst Evaluation; BEA, Zeolite Beta; BTY, Billion Metric Tons per Year; CAPEX, Capital Expenditures; CFPP, Cold Filter Plugging Point; CoMo, Cobalt-Molybdenum sulfided catalyst; CPO, Catalytic Pyrolysis Oil; CSO, Cottonseed Oil; CTO, Catalyst-to-Oil mass ratio; DMDBT, Dimethyldibenzothiophene; DOS, Days on Stream; DTA, Differential Thermal Analysis; EFAL, Extra-Framework Aluminum; EU, European Union; FAME, Free Fatty Acids Methyl Esters; FAO, Food and Agriculture Organization of the United Nations; FCC, Fluid Catalytic Cracking; FPO, Fast Pyrolysis Oil; FTIR, Fourier Transformed Infrared Spectroscopy; GC–MSD, Gas Chromatograph Mass Selective Detector; GHG, Green House Gas; GO, Gas Oil; HAGO, Heavy Atmospheric Gas Oil; HC, Hydrocarbons; HCO, Heavy Cycle Oil; HDA, Hydrodearomatization; HDC, Hydrocracking; HDC_a, Aromatic Hydrogenation; HDM, Hydrodemetallization; HDN, Hydrodenitrogenation; HDO, Hydrodeoxygenation; HDS, Hydrodesulfurization; HDT, Hydrotreating; HMM, High Molecular Mass; HPO, Hydrodeoxygenated Pyrolysis Oil; HVGO, Heavy Vacuum Gas Oil; HVOs, Hydrotreated Vegetable Oils; HYD, Hydrogenation; LAGO, Light Atmospheric Gas Oil; LCO, Light Cycle Oil; LHSV, Liquid Hourly Space Velocity; LMM, Low Molecular Mass; LPG, Liquefied Petroleum Gas; LR, Long Residue; MAT, Micro-activity Test Reactor; MON, Motor Octane Number; MS, Mass Spectrometry; NExBTL, Neste Biomass to Liquid; NiMo, Nickel-Molybdenum sulfided catalyst; NiW, Nickel-Tungsten sulfided catalyst; OPEX, Operating Expenses; PAH, Poly-aromatic Hydrocarbons; PFAD, Palm Fatty Acid Distillate; PIONA, Paraffins, Isoparaffins, Olefins, Naphthenes, Aromatics; REUSY, Rare Earth USY; RON, Research Octane Number; RSO, Rape Seed Oil; SFO, Sunflower Oil; SGO, Standard Gas Oil #4350; SRGO, Straight Run Gas Oil; SRVD, Straight Run Vacuum Distillate; TAN, Total Acid Number; TGA, Thermogravimetric Analysis; TPO, Temperature Programmed Oxidation; TFY, Total Fuel Yield; UK, United Kingdom; USY, Ultra stable Y zeolite (faujasite (FAU) structure according to the International Zeolite Association); VGO, Vacuum Gas Oil; WAF, Waste Animal Fats; WAG, Waste Animal Grease; WCO, Waste Cooking Oil; WHSV, Weight Hourly Space Velocity; ZSM-5, zeolite ZSM-5 (MFI structure according to the International Zeolite Association)

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1. Introduction

The world-wide depletion of crude oil and greenhouse-gases (GHG) emissions associated with the transportation sector has imposed the need for specific energy and climate targets towards energy security and solidarity via a growing decarbonized economy. Particularly for the transportation sector, biofuels are highlighted to play an important role, not only in reducing the associated GHG emissions, but also in enabling the gradual independence from fossil sources, rendering low-carbon-highly-sustainable fuels. Over the last several years, the EU and other countries have established specific action plans for the promotion of biofuels (Directive 2003/30/EC, Renewable Energy Directive 2009/28/EC, Amendment to the Fuel Quality Directive 2009/30/EC, *etc.*). On the 30th of November 2016, the Commission published its so-called ‘Winter Package’ of eight proposals to keep the European Union competitive as the clean energy transition changes the global energy markets. The Commission, backed by the Council, has embraced an ambitious plan for the European Union's electricity market. It will be a major instrument in realizing the transition to a low carbon economy by 2050. This means that EU citizens, as well as industrial users, should gradually switch to electricity not only as a source of light, heating and cooling, but also transportation. That electricity should, in turn, be generated or produced from low carbon sources, including, not only, non-fossil fuels such as hydro, solar and wind energy, but also biofuels, biomass and biogases [1]. It is obvious that biofuels are going to play a very important role in the near future.

The first-generation biofuels (biodiesel and bioethanol) are based on energy crops which limit their environmental benefits (GHG emissions) while leading to incompatibility problems with their fossil-based counterparts and combustion systems. For example, FAME (Free Fatty Acids Methyl Esters) biodiesel, produced via the transesterification of vegetable oils (sunflower, rape, soy, jatropha, *etc.*) has raised economic, environmental and social implications due to the associated “food *versus* fuel” debate, problematic by-products (glycerol) utilization, and fuel quality characteristics. More specifically, FAME's high viscosity, low energy content, high oxygen and water content, as well as high cloud and pour point, render technical limitations regarding its end-use (injector coking in diesel engines, microbial contamination of fuel tanks, quality degradation during long term storage [2–4], *etc.*). Similar limitations are also reported for the first-generation ethanol. Furthermore, air transport has acquired a significant role in the everyday life of the modern world. Consequently, there is increased interest in alternative fuels for aviation [5]. Aviation fuels are characterized by high energy density and, therefore, their production depends mainly on liquid hydrocarbon fuels. Moreover, good flow properties, thermal stability and low freezing are other important criteria that have to be met by alternative aviation fuels [6]. Consequently, FAME biodiesel is not acceptable as an aviation fuel due to its low energy density and high freezing point in comparison with jet fuels.

Due to all these disadvantages of the first-generation biofuels, alternative biofuels technologies are being explored. Today, the involvement of biomass-derived sources into existing petroleum refineries has a growing interest due to the increasing unpredictability of oil prices, environmental concerns (*e.g.,* increasing CO_2 level and climate change), and the necessity to secure an energy supply [7]. Petroleum refineries already have a well-developed infrastructure to produce fuels and base chemicals and, consequently, would not require additional intensive investments for the processing of alternative feedstocks. From this point of view, co-processing of biomass-derived feedstocks with petroleum fractions is an attractive option, which in some cases has found its practical realization already [8–12]. There are two main technologies that could be used for the co-processing of biomass feedstock with petroleum fractions, the first one is *catalytic hydroprocessing* and the second one is *fluid catalytic cracking (FCC)*. Both technologies are found in virtually any conventional refinery, as indicated in Fig. 1.

As far as catalytic hydroprocessing is concerned, it is a well-established and commonly-used refining technology generally employed to upgrade petroleum distillate fractions. There are two types of hydroprocessing technologies: catalytic hydrotreating (HDT) and catalytic hydrocracking (HDC), both of which are normally expected in a typical refinery, as depicted in Fig. 1. The catalytic hydrotreatment process is aimed at removing undesirable heteroatoms such as sulfur, nitrogen and oxygen as well as metals and the partial reduction (hydrogenation) of aromatics. It is applied to intermediate refinery streams which are fed to various conversion units (*e.g.,* FCC feed hydrotreating, naphtha pretreating prior to reforming, *etc.*). Catalytic hydrocracking is a conversion process that mainly aims to reduce the boiling point of petroleum fractions. Its feedstocks are generally heavier petroleum intermediate products