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Co-hydrogenation of fatty acid by-products and different gas oil fractions

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ABSTRACT

It is a great challenge for even the most complex refineries to ensure an economic yield distribution that satisfies the increased diesel fuel and biofuel consumption of the European Union. Thus, it is necessary to investigate the use of different gas oil fractions (e.g. low value streams) for producing diesel fuel blending components and the integration possibilities of biofuel production to a refinery. According to that the co-hydrogenation of mixtures of fatty acid by-products (0–20%) and different gas oil fractions (untreated gas oil fraction, light cycle oil) on commercial, sulphided $NiMo/Al_2O_3$ catalyst was investigated. The effects of feed compositions and process parameters (temperature, pressure, liquid hourly space velocity) on the quality and quantity of the gas oil products were investigated. The applied process parameters were the following: P = 40–70 bar, T = 320–380 °C, LHSV = 1.0–2.0 h^{-1}, hydrogen/feedstock ratio = 600 Nm^3/m^3. We concluded that gas oil boiling range products with high yield can be produced from 10 to 20% fatty acid by-product and 10% light cycle oil containing feedstocks on the studied catalyst. The products are good quality diesel fuel blending components and have high waste derived component content.

1. Introduction

It has long been known that the European Union (EU) supports and encourages the research and use of biofuels. Biofuels are mostly produced from agricultural products, which have high ILUC (Indirect Land-Use Change) risks (European Parliament and Council of the European Union, 2015). That means the whole of the life cycle should be taken into account: direct land use change, growing of feedstocks, biofuel production, transportation, etc. The maximum share of food-based biofuels will be decreased to 3.8% (in energy term) by 2030. Moreover, the share of renewable and low-carbon fuels should be increased to 6.8% (in energy term, including at least 3.6% advanced biofuel) by 2030, too (European Parliament and Council of the European Union, 2016). It is necessary to investigate the production of alternative fuels of which feedstock base (e.g. waste biomass fractions, algae, etc.) does not endanger the food supply security. The research of alternative components (which are applicable in Diesel engines) is very important too due to the importance of diesel fuel in the transportation of the EU. The importance and necessity of alternative fuels are not only justified by the efforts of the EU (lower CO_2 emission during complete lifecycle, environmental prospects, health), but also by the following: the oil stocks are running low and are unevenly distributed around the world. The development and even higher and higher use of alternative fuels could reduce the dependence on crude oil imports and prices. New fuel components are needed to maintain the sustainable development (Ribeiro et al., 2017).

Biodiesel or FAME (Fatty Acid Methyl Esters) is the most well-known biofuel for Diesel engines. This first generation biofuel is produced from different triglycerides (mainly vegetable oils) by transesterification with methanol (possibly ethanol). A large amount of glycerine (~10%) is also produced as a by-product of transesterification. The purification, utilization, sale of glycerine, and producing a product with high added value from it has so many difficulties (Anuar and Abdullah, 2016). Biodiesel has several disadvantages, in case of production and application, too:

- low thermal and oxidation stability due to olefinic double bonds (Pullen and Saeed, 2012),

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Abbreviations

BFA	Fatty Acid-By products
CFPP	Cold Filter Plugging Point
DCO_x	Decarbonylation/Decarboxylation
DMDS	Dimethyl Disulphide
EU	European Union
FAME	Fatty Acid Methyl Esters
FCC	Fluid Catalytic Cracker
HDO	Hydrodeoxygenation
HDS	Hydrodesulphurization
ILUC	Indirect Land-Use Change
LCO	Light Cycle Oil
LHSV	Liquid Hourly Space Velocity
MPY	Main product yield
UGO	Untreated Gas Oil fraction

- bad cold flow properties (high cold filter plugging point) (Knothe, 2010),
- higher fuel consumption compared to fossil diesel fuel (Rahman et al., 2014),
- fatty acid content of feedstocks cannot be too high (Vasudevan and Briggs, 2008), etc.

The maximal limit of biodiesel is 7.0 V/V% from 2013 (EN 590:2013), expectedly it will not change in the future due to the abovementioned negative aspects. Engine manufactures recommend the bio gas oil (hydrogenated triglycerides/fatty acids) instead of biodiesel (ACEA, 2014). It is understandable, because the application of bio gas oil is a good opportunity to replace biodiesel or increase the alternative component content of diesel fuels. Bio gas oil is a paraffinic (n- and iso-paraffins) biofuel in gas oil boiling range, which is produced from the hydrogenation of natural or waste derived triglycerides or fatty acids (Hancsók et al., 2007). The n- and iso-paraffins are the best quality components of diesel fuels from crude oil. Furthermore, bio gas oil has excellent properties (high cetane number, aromatic and sulphur free, etc.).

Bio gas oil containing diesel fuels (blending components) can be produced by two different technological solutions. The first one is the stand alone mode, which means the triglycerides/fatty acids are hydrodeoxygenated in themselves (Hancsók et al., 2012). The product of this process has high cetane number due to its high n-paraffin content (>90–98%), but it has bad cold flow properties, too (high Cold Filter Plugging Point: CFPP). So, it is necessary to improve the cold flow properties of this bio-paraffin mixture by hydroisomerization (Kasza et al., 2014), because the iso-paraffins have about 20–35 °C lower freezing point compared to n-paraffins (in case of the same carbon number). The bio gas oil after this step is blended into a conventional, refined gas oil stream (low sulphur and reduced aromatic content), so that product is a mixture of bio gas oil and conventional diesel fuel. The other technological solution is the co-processing. The pre-treated triglycerides/fatty acids are blended into an untreated refinery gas oil stream, than the quality improvement of the gas oil and the conversion of alternative components are accomplished in one (catalytic) step (Mikulec et al., 2010). The product of this process is a diesel fuel with bio gas oil content, too. If it is necessary, products can also be hydroisomerized.

Nowadays biofuels are mainly produced from crops grown on agricultural land, so the EU will limit the share of these biofuels in the future as it was mentioned above. It is really important to investigate the fuel purpose conversion of waste components for this reason, e.g. waste cooking oil (Dimitriadis and Bezergianni, 2016), waste animal fats (Sági et al., 2016a), etc., but these feedstocks mainly consist of triglycerides and a relatively small amount of fatty acids. Besides the waste oils and fats that contain triglycerides, the fuel purpose hydrogenation of fatty acids is also important. Several researchers reported about the hydrogenation of fatty acids earlier, Kubicková et al. (2005) investigated the deoxygenation reactions of stearic acid, ethyl stearate and tristearine over commercial activated carbon supported palladium. Dodecane was employed as a solvent. It was found that the stearic acid was almost exclusively converted to n-heptadecane (concentration of n-octadecane in the products was negligible) and the higher hydrogen partial pressure suppressed the stearic acid conversion. The conversion increased significantly by increasing the temperature from 300 °C to 360 °C. Madsen et al. (2011) studied the hydrotreating of a model feed consisting of oleic acid and tripalmitin (in molar ratio 1:3) in tetradecane solvent and 5 wt% Pt/γ-Al_2O_3 catalyst was applied. The conversion of reactants was complete at 325 °C already.

The transition metal sulphide catalysts are also a very important type of catalysts from the industrial point of view, because they are suitable for the hydrodeoxygenation of vegetable oils, fats, fatty acids and also for co-processing these components with high sulfuric gas oil fractions. Senol et al. (2007) studied the reactions of methyl heptanoate, heptanol and heptanoic acid on sulphided NiMo/γ-Al_2O_3 and CoMo/γ-Al_2O_3 catalysts. They concluded that the conversion to hydrocarbons was always higher on the NiMo catalyst than on the CoMo catalyst. Coumans and Hensen (2017) studied the hydrodeoxygenation of model compounds (methyl oleate, oleic acid and trinolein) over sulphided NiMo/γ-Al_2O_3. They found that the conversion of the model compounds to paraffins was hardly affected by H_2S, water, CO and tetralin solvent. Boonyasuwat and Tscheikuna (2017) studied the co-processing of palm fatty acid distillate (0–25%) and light gas oil over commercial CoMo/Al_2O_3. They observed significant heat effect due to highly exothermic reactions, when the feedstock contained 25% palm fatty acid distillate. The conversion of palm fatty acids was high in all cases (>98%). The sulphur content of the products did not satisfy the requirements of diesel fuel standard (EN 590:2013).

The abovementioned research work focused on the reactions of the model fatty acid molecules and their derivates and did not investigate the quality of the products. The hydrogenation of fatty acids in real gas oil fractions and the quality of the products from the point of view of diesel fuel standard requirements were investigated by only a very few papers. It would be desirable to investigate the applicability of real waste derived feedstocks and gas oil fractions too, because it could give more accurate results and information. These results would be important from the industrial point of view, too. The application of these compounds could also contribute to the satisfaction of the abovementioned targets.

Not only the production and even higher and higher application of biocomponents of diesel fuel are huge challenges for the European oil companies, but also it is not so easy to ensure the economic production of conventional diesel fuel, either. Due to the fact that dieselization takes place in the EU, in other words proportionally the demand for diesel fuel is expected to increase compared to gasoline (BP, 2016) till 2020, refineries are trying to satisfy this increased demand the most economical way. A possible solution for FCC (Fluid Catalytic Cracker) based refineries is to increase their light cycle oil (LCO) yield. This refinery stream is usually blended to heating oils, due its low quality (cetane number $\leq$ 25, high aromatic content 70% <, etc.) and value (Sharafutdinov et al., 2012). Quality improvement of light cycle oil is needed for the utilization as a diesel fuel blending component. During the hydrogenation of LCO a large amount of heat is generated due to the very exothermic