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Research article

Diesel fuel blending components from mixture of waste animal fat and light cycle oil from fluid catalytic cracking

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ABSTRACT

Sustainable production of renewable fuels has become an imperative goal but also remains a huge challenge faced by the chemical industry. A variety of low-value, renewable sources of carbon such as wastes and by-products must be evaluated for their potential as feedstock to achieve this goal. Hydrogenation of blends comprising waste animal fat (≤70 wt%) and low-value fluid catalytic cracking light cycle oil (≥30 wt%), with a total aromatic content of 87.2 wt%, was studied on a commercial sulfided $NiMo/Al_2O_3$ catalyst. The fuel fraction in the diesel boiling range was separated by fractional distillation from the organic liquid product obtained from the catalytic conversion of the blend of 70 wt% waste animal fat and 30 wt% light cycle oil. Diesel fuel of the best quality was obtained under the following reaction conditions: T = 615–635 K, P = 6 MPa, LHSV = 1.0 h^{-1}, H_2/feedstock ratio = 600 Nm^3/m^3. The presence of fat in the feedstock was found to promote the conversion of light cycle oil to a paraffinic blending component for diesel fuel. Thus, a value-added alternative fuel with high biocontent can be obtained from low-value refinery stream and waste animal fat. The resultant disposal of waste animal fat, and the use of fuel containing less fossil carbon for combustion helps reduce the emission of pollutants.

1. Introduction

Dieselization (BP, 2017) of passenger cars was an important trend in the European Union (EU) but is now beginning to decline (ACEA, 2016). Nevertheless, the demand for diesel fuel remains higher than that for gasoline, and is expected to increase by about 45% until 2040 (ExxonMobil, 2016) due to the increasing energy demand of heavy-duty vehicles. Given this significant imbalance, it is essential for European refineries to shift their product portfolio towards middle distillates. Besides meeting the increased demand for diesel fuel, European refineries face the additional challenge of following the EU directive that requires alternative energy components to constitute at least 10% of transportation fuels (European Parliament, 2009). Currently, biodiesel (fatty acid methyl esters) is the most commonly employed biocomponent in diesel fuels. It is derived mainly from edible oils. Compared to traditional diesel fuel, biodiesel has many disadvantages such as low thermal and oxidation stability (Pölczmann et al., 2016), bad cold flow properties (Anwar and Garforth, 2016), and low energy content (Rahman et al., 2014). It is noteworthy that the EU aims to increase the share of renewable and low-carbon fuels in its energy mix (European Parliament, 2016). The energy target set for the use of advanced biofuels, waste-based fuels, and renewable electricity is 1.5% and 6.8% (including at least 3.6% for the use of advanced biofuels) by 2021 and 2030, respectively. Given their limited availability, food-based biofuels are expected to account for no more than 7% of the total portfolio of advanced biofuels by 2021; this is slated to decline to 3.8% by 2030. Conscious environmental management which is a pillar for sustainable development can be significantly contributed to achieving these goals (Mikulčić et al., 2017).

The production and use of bio gas oils is a potential solution to the rising demand for high-quality diesel fuels. Bio gas oil is a mixture of n- and iso-paraffins in the gas oil boiling range produced by special hydrocracking (hydroconversion) of natural and waste-derived esters (mono-, di- and triglycerides) and fatty acids (Fig. 1) (Hancsók et al., 2007). Bio gas oil is an excellent blending component for diesel fuel because of its high cetane number and the absence of aromatic and sulfur-based components among other desirable characteristics (Kovács et al., 2011). There are no regulatory restrictions imposed on the blending of bio gas oil with diesel fuel. Moreover, if the bio gas oil is produced from waste-derived esters or fatty acids, its usage contributes doubly to meeting the regulatory requirement of having 10% of constituents from renewable sources in the fuel product.

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Abbreviations and nomenclature list

CFPP	cold filter plugging point
DCOx	decarbonylation/decarboxylation
EU	European Union
FCC	fluid catalytic cracking
HDO	hydrodeoxygenation
HDN	hydrodenitrogenation
LCO	light cycle oil
WAF	waste animal fat
T	temperature [K]
P	pressure [Pa]
LHSV	liquid hourly space velocity [h^{-1}]

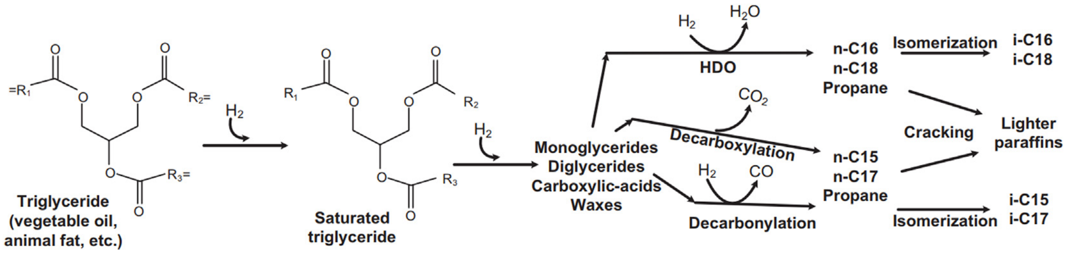

Fig. 1. Reaction routes of bio gas oil production (Huber et al., 2007).

Catalytic hydrogenation of natural (Asikin-Mijan et al., 2017) and/or waste-derived esters (chiefly triglycerides), and/or fatty acids (Mikulec et al., 2010) has been studied by several authors. The co-processing of esters with different straight-run (distilled) gas oils e.g. vacuum gas oil (Huber et al., 2007); heavy atmospheric gas oil (Rana et al., 2013) and light gas oil (Boonyasuwat and Tscheikuna, 2017) has attracted attention in recent times. Various studies have established that bio gas oils or diesel fuels containing bio gas oil are of good quality (Tóth et al., 2011), but they have high cold filter plugging points (CFPPs), in the range 275–300 K, due to their high n-paraffin content. This problem can be eliminated by hydroisomerization of the products e.g. on Pt/SAPO-11 catalyst (Hancsók et al., 2011) or on NiW/zeolite catalyst (Bezergianni et al., 2014). Most studies have focussed on hydrogenation of vegetable oils but there is growing research interest in waste-derived triglycerides e.g. waste cooking oil (Wang et al., 2017).

The processing of crude oil generates a by-product known as fluid catalytic cracking light cycle oil (FCC LCO), which is a component of very low value. Its characteristics such as high density, total aromatic content of 60–90 wt% of which polyaromatics constitute 45–50 wt%, low cetane number ($<$ 25), and high sulfur and nitrogen content depending on the FCC feedstock, rendering it unsuitable for blending with diesel fuel unless its quality is enhanced (Sharafutdinov et al., 2012). In addition to the removal of sulfur and nitrogen, it is also essential to hydrogenate the aromatic constituents of FCC LCO to produce blending components that exhibit good combustion properties (Srivastava and Hancsók, 2014).

Only a few studies focus on the co-processing (co-hydrogenating) of LCO and triglycerides. Yungi (2009) investigated the co-hydroprocessing of soybean oil (10–30 wt%) and LCO on a NiMoP/γ-Al_2O_3-HUSY catalyst, and found that the cetane number of the products increased by 1.8–6.5 compared to those obtained from the LCO hydrogenated without soybean oil. Wang et al. (2015) studied the co-processing of LCO and 5.0–7.5 wt% canola oil on a commercial NiMo/Al_2O_3 catalyst. Using the characteristics of the hydrogenated LCO as reference, it was concluded that the paraffin produced from the triglycerides increased the cetane index of the products by 2.5–4.0. However, the cold flow properties of the products deteriorated concurrently. In the aforementioned studies, edible vegetable oils were blended only in small quantities (5.0–7.5 wt% of canola oil and 10–30 wt% of soybean oil) relative to the LCO. Moreover, the co-processing of LCO and waste animal fat (WAF) has not yet been investigated in detail.

It is important to develop technology to produce high-value blending components for diesel fuel from blends of WAF and LCO. The present study is a contribution to this objective. Based on theoretical considerations it has been concluded that the favourable properties of n-paraffins from WAF can compensate the unfavourable properties of aromatic compounds remaining after LCO hydrogenation. An additional goal was to specify a catalytic system (i.e. catalyst, advantageous process parameters) capable of producing blending components of good quality for diesel fuel (sulfur and nitrogen $\leq$ 10 mg/kg, polyaromatics $\leq$ 8.0 wt%, cetane index $\geq$ 46) with a high proportion of bio-components.

2. Experimental

2.1. Feedstocks

We investigated the heterogeneous catalytic hydrogenation of blends of WAF ($\leq$70 wt%) and FCC LCO ($\geq$30 wt%) on a sulfided commercial NiMo/Al_2O_3 catalyst. We used WAF from a protein processing plant and LCO from a fluid catalytic cracker (from MOL Plc.) for the catalytic hydrogenation experiments. The properties of the feedstocks are summarised in Tables 1–3. Dimethyl disulfide (purchased from Sigma-Aldrich) was added to the feedstocks to increase their sulfur content to 1000 mg/kg to preserve the sulfide form of the NiMo/Al_2O_3 catalyst during the reaction.

2.2. Analytical methods

The properties of the feedstocks and the products were determined and calculated according to the test methods specified in the EN 590:2017 standard with the given precisions (Table 4). The chemicals used in the analytical methods had been purchased from Sigma-Aldrich. The hydrocarbon composition of the products was determined by gas chromatography (Shimadzu GC, 2010). The applied column was stable at high temperatures (Restek MXT-1, 30 m × 0.28 mm × 0.1 µm). The

Table 1
Properties of waste animal fat.

		Fatty acid composition, wt%	
Density at 323 K, g/cm^3	0.8838		
Acid number, mg KOH/g	0.85	C14:0	2.1
Water content, mg/kg	5629	C16:0	23.4
Metal content, mg/kg		C16:1	2.8
Ca	196	C18:0	16.3
Mg	29	C18:1	40.2
K	61	C18:2	7.5
Na	70	C22:1	7.6
Phosphorus content, mg/kg	164		
Nitrogen content, mg/kg	38		