



Straight run gas oil as sulphur compound to preserve the sulphide state of the hydroprocessing catalyst of triglycerides



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ARTICLE INFO

Article history:

Received 21 December 2014

Received in revised form

30 July 2015

Accepted 30 July 2015

Available online 6 August 2015

Keywords:

Biofuel

Diesel fuel

Paraffinic diesel

Triglyceride

Hydrogenation

ABSTRACT

The hydrogenation of natural triglycerides to produce motor fuels has an increasing importance. Therefore increase the efficiency of the production is important. So a special case of hydrogenation of triglycerides was studied on a sulphided NiMo/Al₂O₃ catalyst at wide range of process parameters (Pressure = 40 and 80 bar, Temperature = 320–380 °C, Liquid Hourly Space Velocity = 0.75–2.0 h⁻¹, H₂/feed ratio = 600 m³/m³). The sulphur content of the feedstock was ensured with mixing a small amount (10%) of high sulphur containing (0.9%) gas oil into the sunflower oil to ensure the sulphided state of the catalyst. In comparison, the hydrogenation of a reference feedstock was examined which sulphur content was set to similar concentration (905 mg/kg) level by using an easily decomposable sulphur compound (dimethyl disulphide). By applying favourable process parameters (Temperature = 360–380 °C, Pressure = 80 bar, Liquid Hourly Space Velocity = 0.75 to 1.0 h⁻¹, H₂/feed ratio = 600 m³/m³) the properties of the products being obtained in high yield satisfied the requirements of the EN 590:2013 standard, except Cold Filter Plugging Point and density values for both feedstocks. In case of the catalytic hydrogenation of triglycerides it was concluded to cover the sulphur content of the feedstock with straight run (high sulphur containing) gas oil is a suitable and cost-effective solution to preserve the sulphide state of the catalyst. Diesel fuel can be produced with blending of products of high cetane and low density into other gas oil streams. The hydrogenated vegetable oil products can improve the quality of low-quality gas oil streams to produce better quality diesel fuel with bio-component content.

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1. Introduction

In case of motor fuel production the use of alternative and bio-derived blending components in higher amount is encouraged by the European Union with directives. Until 2020, the use of bio fuels is specified in 10% referred to the energy content of motor fuels used in the transport sector (Renewable Energy Directive, 2009/28/EC). In addition, they urge to take into account the impacts of the indirect land use change (ILUC) in calculation of greenhouse gas (GHG) emissions (Schmidt et al., 2015) (2009/30/EC). The EU has supported the production of fuels derived from waste from the beginning. Nowadays, the limitation of using the first generation biofuels derived from edible feedstocks is also discussed. Currently the first generation motor fuels produced from edible feedstocks are in use simultaneously with the waste-derived fuels (Eguchi

et al., 2015). The aim of further developments is the use of algae oil and lignocelluloses as feedstock (Liew et al., 2014).

Nowadays, because of the efforts of the EU and several disadvantages (hydrolysis sensitivity, polymerization, etc.) of first generation fatty acid methyl esters obtained by transesterification of triglycerides (vegetable oils, fats, etc.) the demand for these products is continuously decreasing. Their place will be taken over by the second generation bio gas oils (HVO: hydrogenated vegetable oil, mixture of normal and isoparaffins) produced by catalytic hydrogenation (Srivastava and Hancsók, 2014).

Several companies from the oil and automotive industry created the CWA 15940:2009 standard for the HVOs and other synthetic fuels: "Automotive fuels – Paraffinic diesel from synthesis or hydrotreatment – Requirements and test methods". The standard defines two quality classes for the paraffinic diesel fuels (with high and normal cetane number) (Table 1). In comparing to the requirements of the EN 590:2013 (standard for the fossil diesel fuel) the paraffinic diesel should satisfy some other properties too. The cetane number of the paraffinic diesel is considerable higher than

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Table 1
Main specifications of the diesel fuels by the standards.

Property	Unit	CWA 15940:2009				EN 590:2013	
		Class A		Class B		min.	max.
		min.	max.	min.	max.		
Cetane number		70.0	–	51.0	66.0	51.0	–
Density at 15 °C	kg/m ³	770	800	770	800	820	845
Density at 50 °C (calculated)	kg/m ³	744	775	744	775	796	822
Total aromatics content	m/m %	–	1.0	–	1.0	–	–
Polycyclic aromatics content	m/m %	–	0.1	–	0.1	–	8.0
Total olefin content	m/m %	–	0.1	–	0.1	–	–
Sulphur content	mg/kg	–	5.0	–	5.0	–	10.0
Flash point	°C	>55	–	>55	–	>55	–
Viscosity at 40 °C	mm ² /s	2.00	4.50	2.00	4.50	2.00	4.50
Distillation 95%, (V/V) recovered at	°C		360		360		360

the cetane number of fossil diesel's, because the n-paraffins provide the highest ones among the hydrocarbons. The density is lower because of the carbon chain length of the triglycerides. The paraffinic diesel is almost aromatic and sulphur free. Because of these favourable properties the HVOs are preferred as bio-components, so the EN 590 standard does not limit their concentration in the diesel fuel.

For the special hydrogenation of the triglyceride (preferably waste-derived) containing feedstocks researchers investigated multiple catalysts with different compositions. Chistyakov et al. (2013) studied platinum and palladium containing Al₂O₃ and zeolite supported catalysts for converting rapeseed oil. Platinum (as active metal) catalysts were used to convert triglycerides on Al₂O₃ (Madsen et al., 2011) and SAPO-11 (Herskowicz et al., 2013) support too. Krár et al. (2010, 2011) studied the conversion of sunflower oil on reduced state (non-sulphided) conventional CoMo/Al₂O₃, and in addition on CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts. Hancsó et al. (2012) found that the hydrogenation activity of the catalysts in reduced state (non-sulphided) increasing by the following order NiW/Al₂O₃ < NiMo/Al₂O₃ << CoMo/Al₂O₃. The triglyceride containing feedstocks on sulphided catalysts can also be converted, for which e.g. CoMo/Al₂O₃ (Wei-qian et al., 2013), NiMo/Al₂O₃ (Sri et al., 2014) and NiW containing (Mikulec et al., 2010) catalysts were suitable. Veriansyah et al. (2012) compared several catalysts for hydrogenation of soybean oil; they achieved the highest conversion using a sulphided NiMo/Al₂O₃ catalyst. Transition metals (NiMo and NiW) on SAPO-11 support are suitable to hydroprocess of vegetable oils to hydrocarbons, but due to the high hydrocracking activity of the zeolites the yield of the diesel fraction decreased about to 40% (Verma et al., 2015).

In summary, the noble and transition metal catalysts on various supports are suitable for processing of the triglyceride containing feedstocks. Catalysts containing noble metal have high activity, but they are expensive and quickly lose their activity. Transition metal catalysts in reduced state – like the noble metal catalysts – do not require the increase in the sulphur content of the feedstock, but they less active than in their sulphided state.

Beside of processing of feedstocks in themselves, the importance of co-processing of the triglycerides from different origin with straight run gas oils in existing refinery plants with catalytic hydrogenation directly into bio component containing diesel fuel is increasing. Our research group previously studied the hydrogenation of 0, 5, 15 and 25% sunflower oil containing gas oils to produce clean diesel fuel (Tóth et al., 2011). Furthermore, application of waste cooking oils as feedstock components at co-processing is also possible (Bezergianni et al., 2014a).

Among the catalysts investigated by researchers and applied in the industry, the transition metal/support catalysts in sulphide

state have proven to be the most suitable for the processing of the triglycerides in themselves and by combining with gas oils. To maintain the activity of the catalyst being in sulphide state the addition of sulphur, which is continuously “washing down” (balance between the catalyst and the fluid), is required from external source (Gong et al., 2012) (approx. 400–2000 mg/kg of hydrogen sulphide in the reactor). In case of processing of pure triglycerides the necessary sulphur can be added into the catalytic system with the feedstocks: easily decomposable sulphur compounds (van Heuzen et al., 2007) (e.g. DMDS) are added to the liquid feed, or hydrogen sulphide (Brevoort et al., 2006) is added to the hydrogen feed. In the case of co-processing, triglycerides (in the sufficient amount) are usually added to the gas oil to ensure the second-generation bio-component content of products. The sulphur content of these gas oils are as high as to provide the required concentration of sulphur.

During processing triglycerides in themselves the application of a special case of co-processing has not been studied yet, in which only a small amount (5–15%) of straight run (high sulphur containing) gas oil is added to the feedstock to cover the required sulphur content, and maintaining the active (sulphided) state of the catalyst. The external addition of sulphur is required because even in case of using gas recirculation a part of the product gases has to be purged, which reduces the amount of sulphur in the system as well.

2. Materials and methods

Experiments were carried out to hydrogenate two sunflower oils, those contain different sulphur sources, applying wide range of process parameters. The effect of the application the different sulphur sources on the yield and quality properties of the main products was investigated.

2.1. Feedstocks

For the hydrogenation experiments two different feedstocks were used (Table 2). Sunflower oil (SO) and straight run gas oil (GO) were used to prepare the feedstocks. The sunflower oil – originated from Hungary – was properly pretreated by filtering through cotton filter cloth and filter paper in one step applying a pressure filter equipment. The straight run gas oil was produced from Russian crude oil by the MOL Hungarian Oil and Gas PLC.

The main sunflower oil feedstock (TUE2) had a small amount (10%) of high-sulphur (0.9%) gas oil content (total sulphur content: 900 mg/kg). In comparison, an other feedstock (TUE1) was examined, which sulphur content was set to similar concentration level (905 mg/kg) with dimethyl disulphide (DMDS) (Table 2).

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