



Hydroprocessing of fatty acid methyl ester containing resin acids blended with gas oil



Shanmugam Palanisamy, Börje S. Gevert*

Chalmers University of Technology, Göteborg, Sweden

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ABSTRACT

Fatty acid methyl ester (FAME) with resin acids was blended with light gas oil (LGO) from 10 to 30 wt.% and then investigated using elevated temperature (300 to 370 °C) at 5 MPa on NiMoS/alumina in a trickle-bed reactor (TBR). Hydroprocessing of blended LGO showed lower S content (less than 8 ppm) at 100% conversion and reached the target cloud point on middle distillate diesel fuel. In this study a significant change in the physical and chemical properties of LGO was observed. For the distillate product, viscosity, distillation curve, nitrogen content and density were all in the expected standard grades of diesel. Here, a presence of sulfur in LGO significantly reduced catalyst deactivation. Higher concentrations of aromatic content and polycyclic aromatic hydrocarbons degraded to reach the EU diesel standard; in particular, the resin content in FAME could enable up to 50% aromatization. Elevated experimental temperatures increased decarboxylation as compared with deoxygenation for all compositions of FAME and resin acids in this upgrading process. Carbonyl compounds like CO and CO₂ formation in lighter products result from resin acids decarbonylation and decarboxylation reaction pathway.

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1. Introduction

The on-road legislation by EU member states is in force from 2012 for gas oil's and diesel's sulfur not to exceed 10 ppmw. A large number of studies have investigated desulfurization of middle distillates to adopt in EU member states refineries. It achieved an impressive milestone on commercialization of the hydrodesulfurization (HDS) process, particularly for middle distillate in refineries. These middle distillate fuels were vital for the transportation sectors [1–4]. One of the middle distillates – light gas oil (LGO) – had a high value because of properties and energy content that were dependent on natural and fuel adaptability. The cetane number was the main property that needed to be considered in the qualitative analysis to substitute renewable fuel with LGO [5–8]. The current standard cetane index of EU is at the range of 46 to 51 according to EN 596 standards. Sometimes, the premium diesel exceeds as high as 60. Addition of carbon rich substitutes like FAME increases cetane number. An increase in the cetane number of LGO resulted in a lower of shorter ignition delay, which tended to lessen combustion noise, leading to increased energy

efficiency and power output for power engines [9]. However, an increase in cetane number proved to be non-friendly for easier starting in severe winter weather and reduced both smoke and odor, which is in need of upgrading further [9–11]. Although kerosene and turbine fuels have similar properties (such as LGO), they had different specifications corresponding to their intended use. LGO mostly had paraffin and olefin type hydrocarbons with a boiling range between 125 and 300 °C, sometimes mixed with various cracked distillate fractions to increase volume requirement [12–14]. An increase in octadecane (C₁₈) and heptadecane (C₁₇) in production by hydrodeoxygenation (HDO) of fatty acid methyl ester (FAME) in LGO gives a better cetane number for diesel fuel compared to if no n-C₁₇ and n-C₁₈ was added [15–17].

Presently, combining HDO and HDS in ultra-low sulfur diesel production is recognized in some refineries through NiMoS catalyst [4,18]. Resin acids (e.g., abietic acids) present in tall oil were the main renewable sources. These acids have a complication of tri-ring structure making hydrogenation difficult in downstream products [7,19]. A primary aim of research has been to understand the fundamental aspects of the NiMoS catalytic reaction [18,20–23], develop/design a suitable condition and demonstrate the physico-chemical properties of deoxygenation products rich in carbon content [7,24]. The main objective of this study was to examine the effect of hydroprocessing FAME with resin acids (FAME-resin) blended with LGO (referred to as middle distillates). In this study, LGO was blended with FAME-resin and hydrogenated on a NiMoS catalyst for temperatures ranging between 300 and 370 °C at 5 MPa and H₂/feed (mln/mln) = 80.

* Corresponding author at: Ecotraffic ERD³, Kempross AB, Larsereds lyckor 14, 42539 Hisings kärri, Sweden. Tel.: +46 702195834.

E-mail address: gevert@ecotraffic.se (B.S. Gevert).

2. Experimental

2.1. Feed material

The feed contained 78% FAME and 20% resin acids of the carboxylic group on tri-ring cyclic hydrocarbon with the rest as neutral fractions. The classified fatty group with resin acids is shown in Table 1. The feed was FAME-resin blended with LGO with three ratios: 10, 20 and 30 wt.%. The properties of the LGO were aromatic content 17.8 (v/v %), sulfur (S) content 295 (ppmw) and paraffin fraction from C₈ to C₁₆. Table 1 provides additional information about the LGO.

2.2. Reactor system

A fixed trickle-bed and semi-batch reactor with a sulfidized NiMo/alumina catalyst was investigated. The major reaction parameters included liquid hourly space velocity (LHSV = mln of liquid/ml of cat. * h), feed mixture, hydrogen flow and reaction temperature (T) (°C). For the investigation, the commercial catalyst Trilobe HDN-60 (NiMo/ γ -Al₂O₃) from Criterion Catalysts was used and consisted of NiMo/ γ -Al₂O₃ with 2.5–3% Ni and 12.5–13.5% Mo with 83–85% γ -Al₂O₃. The catalyst had the shape of 1/32-in extrudes with a surface area of 156 m²/g and a pore size of 7–8 nm calcined at about 400 °C for overnight: 31 ml (27.43 g) was loaded in the center of trickle-bed reactor (TBR) for in-situ sulfidation. The catalyst was heated to 400 °C at the rate of 10 °C per minute and the temperature maintained for 2 h under nitrogen flow of 100 mln per minute before sulfidation. Later, sulfidation was achieved by allowing H₂S as 10% by volume of S in H₂ at 200 mln per minute for 3 h and kept overnight under a small nitrogen flow. At 360 °C and 5 MPa, LGO was flooded for 10 days, until stabilized coke developed over catalyst and steady state was achieved for further experimentation.

The reactor set-up consisted of a feed tank, Dossier pump, TBR, separator tank, gas meter and collector. The down flow TBR, insulated with three independent heating zones, had an internal diameter 1.8 cm, with borosilicate glass pellets of 2 mm in diameter filled in void space. The feed that was fed by the reciprocal dossier pump was mixed with H₂ or N₂ gas before being allowed on a co-current flow into the reactor: all products were withdrawn periodically from the separator tank [25].

The experiment used a semi-batch reactor made up of stainless steel with 300 ml capacity that was connected to a gas inlet and outlet. The thermo couple, heating system and magnetic stirrer was integrated in an eight microprocessor-based process controller to maintain the operating condition steadily. The experiments were carried out with the same stirring speed. In this reactor, 5 wt.% abietic acid in hexadecane was used at temperatures of 300 to 350 °C and 5 MPa experimented on a NiMoS/alumina catalyst. The reactor was loaded with 150 ml of solution that includes 1 g of a defined amount of NiMoS catalyst and 3 g of tetradecane as internal standard.

The product collected from the reactor was placed in the distillation re-boiler on N₂ flow at 100 mln per minute. The simple distillation column consists of 2 L capacity re-boiler and heated to a desired

temperature for removal of water and lighter hydrocarbons from the downstream product at a cut point temperature of 162 °C. The residue was analyzed to check for essential features of physico-chemical properties.

2.3. Analysis

Simulated distillation [SIM-DIST] (ASTM D2887) was performed on the upgraded product by gas chromatograph (GC) technique. Data computation was performed with a Varian 4270 integrator. The flue gas from the reactor was collected in a gas bottle at ambient condition and subsequently analyzed using the Clarus 500 online GC. This GC has an inlet and outlet sampling valves with a thermal conductivity detector (TCD) and flame ionization detector (FID), as well as four valves actuated by nitrogen gas at 0.4 MPa. The detector out signal was connected with a 600 link switch controller that interprets the signal to an integrator. The detectors are TCDs for analyzing CO, CO₂ and CH₄, and FID for lighter hydrocarbon fractions. Helium was used as carrier gas for the TCD, which was maintained at 200 °C with oven heat-up of 40 to 60 °C at 2 °C per minute and nitrogen as carrier gas for the FID at 60 °C as oven temperature.

The cloud point, aromatic content, density, nitrogen content, sulfur content, SIM-DIST and viscosity properties were analyzed from the residue, which was performed by Preem refinery, Sweden.

3. Results and discussion

3.1. Remarks

In all experiments, the general hydrogenation of FAME produced normal hydrocarbons (e.g., n-C₁₇ and n-C₁₈) as reported in previous studies [26,27]. The ratio of liquid to gas inlet was held constant throughout the experiments with comparability of mass balance and thermodynamic calculation. Molar balances based on the gas product analyses were calculated (error elimination was less than 5% on average). The assumption regarding hydrogenation includes deoxygenation and cracking, which were summed in the result description. The recovered residue of products mainly contains hydrocarbons between octane and octadecane with traces of high hydrocarbons. Moisture content in the products was excluded.

3.2. Aromatic composition

The feed of three compositions were tested at elevated temperatures and space velocity in the TBR. The aromatic content in resin acid was done in order to study the intra-couple of deoxygenation and de-aromatization process in ensuring the product property. LGO contains 17.8 vol.% aromatics by the addition of FAME-resin aromatic compositions and retained at 17.7 vol.% for all three feed types. The upgraded products have aromatic content between 17 and 18 vol.% (see Table 2) for different blended feed compositions. This observation led us to understand that there was neither notable aromatization nor cyclic scission. However, reaction mechanism

Table 1
Classified composition of resin acids with fatty acid methyl esters supplied by Preem AB.

Components	wt%	Components	wt%	Components	wt%
Octadecadienoic acid C ₁₈ :2	1.25	Isopimaric acid	1.37	β -Sitosterol	0.16
Octadecenoic acid C ₁₈ :1	0.80	Levopimaric acid	0.21	Squalene	0.34
Octadecanoic acid C ₁₈ :0	0.28	Palustric acid	1.32	Other	1.79
Methyl palmitate	2.82	Neobietic acid	0.34		
Methyl linolenate	6.77	Dehydroabietic acid	4.45		
Methyl linoleate	35.75	Sandaracopimaric acid	0.42		
Methyl oleate	16.26	Pimaric acid	2.40		
Other esters	14.05	Abietic acid	8.69		
Total free fatty acids and esters	78.41	Total resin acids	19.29	Total neutrals	2.29

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