

## Bio-paraffin mixtures production over different catalysts

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### Abstract

The hydrocarbons of bio-paraffin mixtures are mostly in diesel fuels (less in aviation fuels) boiling range; therefore they can be promising alternative fuel component. Moreover, the bio-paraffin mixture can be used in the cosmetics and pharmaceutical industry, food industry, in petrochemical industry, for example C14-C18 paraffin hydrocarbons can play important role in detergent production (e.g. for lubricant or household detergents). The main production possibilities of bioparaffins are the followings: integrated Fischer-Tropsch (F-T.) synthesis from biomass derived syngas, from lignocellulose through simple sugars, from bioethanol via dehydrogenation, oligomerization and saturation, from natural/waste triglycerides, from natural/waste fatty acids. The aim of our research was the investigation of (catalytic) hydrogenation of waste fatty acid mixture over different catalysts (sulphided or non-sulphided CoMo/Al<sub>2</sub>O<sub>3</sub>, NiMo/Al<sub>2</sub>O<sub>3</sub>, and Pt/Al-SBA-15 to valuable bio-paraffin for JET/diesel fuel blending components, petrochemicals or other valuable products). We investigated the effects of catalytic system (reactor, catalyst properties, process parameters – temperature: 250-350 °C, pressure: 40 bar, liquid hourly space velocity: 1,0-3,0 h<sup>-1</sup>, hydrogen/feedstock volume ratio: 450 Nm<sup>3</sup>/ m<sup>3</sup>) on the yield and quality (e.g. chain length, isoparaffin content, content of non-paraffinic components) of the paraffin mixture and they applicability. We carried out the catalytic (hydrogenation) experiments in a (pilot scale) high-pressure reactor system, which contained a tubular down flow reactor with 100 cm<sup>3</sup> effective volume and all the equipment and devices applied in the reactor of an industrial hydrotreating plant. The properties of the feedstocks and the products were determined by standardized methods and they composition with gas chromatographic method, respectively. Based on the obtained results, all the catalysts are suitable for production of bioparaffins from waste fatty acids. Yields of main products changed in function of catalyst compositions (sulphided NiMo/Al<sub>2</sub>O<sub>3</sub> > sulphided CoMo/ Al<sub>2</sub>O<sub>3</sub>) > non-sulphided NiMo/Al<sub>2</sub>O<sub>3</sub> ≥ non-sulphided CoMo/Al<sub>2</sub>O<sub>3</sub> > Pt/Al-SBA-15). The paraffin mixtures with relatively high isoparaffin content were obtained over non-sulphided CoMo/Al<sub>2</sub>O<sub>3</sub> and Pt/Al-SBA-15 catalysts.

Biofuels and bio blending components have higher and higher importance because of their economic and environmental advantages both in Europe and on the other parts of the World [1-2]. Mainly the second generation ones

have very favourable composition, since they are practically free of sulphur and nitrogen, and their olefin and aromatic content is close to zero. They contain mainly iso and normal paraffins which have very favourable performance properties. Consequently during their combustion environmentally and toxicologically harmful compounds (SO<sub>x</sub> and NO<sub>x</sub>) do not form, their combustion is clear (low particle emission), furthermore the greenhouse gas emission is significantly lower relative to the whole life cycle [3]. Nowadays mainly the mixture of fatty acid methyl esters (biodiesels) are used as biocomponents of Diesel fuels which are produced from different vegetable oils and used cooking oils by transesterification with generally methanol.

But these have numerous disadvantages such as they form deposits in the fuel supply system and the combustion chamber, they have poor storage (heat and oxidation) stability because of the olefinic double bonds of the molecules, they tend to water uptake, the esters bond tend to be hydrolysed resulting corrosive acids, they shorten the oil change interval, etc. [4]. Consequently in the European Union the maximum blending quantity of fatty acid methyl esters into Diesel fuels was limited to 7.0 v/v% by the EN 590:2009 standard based on the proposition of the vehicle manufacturers. At the same time the use of at least 10% of bio origin component is a target up to 2020 in the EU. Because of these disadvantages and of the quantity of bio-origin fuels can be increased from the natural triglycerides (conventional and improved vegetable oils, used cooking oils and fats, greases from meat and leather processing industry, “brown grease” of sewage farms, etc.) such kind of fuel components have to be produced which molecular structure differs from that of the fatty acid methyl esters.

This kind of compounds are hydrocarbons produced by heterogeneous catalytic hydrogenation of triglycerides, consisting mainly from mixtures of normal paraffins, consequently they have not possess with the disadvantageous properties of biodiesels [4]. However the cold flow properties of these mixtures rich (>95%) in normal paraffins (mainly n-C12-n-C20) are unfavourable (the freezing point of normal paraffins is high, e.g. n-C18: +28 °C). This characteristic generally can be improved by addition and/or isomerization. But the currently used flow improver additives were not effective enough in case of these products of new composition.

### *Extended Abstract*

Accordingly the isomerization seems to be the suitable finishing process step to produce mixtures with good cold flow properties and high cetane number [4, 6-7]. The composition of the mainly n-C12-n-C20 mixtures obtained by the fuel purpose hydrogenation of triglycerides can be significantly different depending on the used feedstock and catalytic system (catalyst, process parameters) [4, 8-12]. The oxygen removing reactions change as a function of the catalyst and process parameters.

For example at elevated temperature and on higher acidity catalyst the decarboxylation reaction 364 became dominant resulting shorter hydrocarbon chain by one carbon number than that of the fatty acid. Side reactions also take place during the oxygen removal. For example by increasing the severity of operational parameters the cracking reactions become dominant, furthermore the aromatization may also take place over high activity catalysts or at high temperature. Accordingly the aim of present paper was the investigation of the effect of feedstock on the hydroisomerization of normal paraffin rich (>95%) mixtures (produced from sunflower oil) over 0.5% Pt/SAPO-11 catalyst.

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