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Quality improvement of bio-paraffin mixtures

Tamás Kasza [a], Dénes Kalló [b], Jenő Hancsók [c,*]

[a] MOL Hungarian Oil and Gas Plc., P.O. Box 1, H-2443 Százhalombatta, Hungary
[b] Institute of Materials and Environmental Chemistry, Research Center for Natural Sciences, Hungarian Academy of Sciences, P.O. Box 17, H-1525 Budapest, Hungary
[c] University of Pannonia, Department of MOL Hydrocarbon and Coal Processing, P.O. Box 158, H-8200 Veszprém, Hungary

HIGHLIGHTS

- Quality improvement of bio-paraffin by isomerization was studied to produce biogasoil.
- Reaction rates and activation energy of isomerization were investigated over Pt/SAPO-11 catalyst.
- The effect of fatty acid content of feedstock on isomerization reactions was demonstrated.
- Industrial application of favourable results and excellent quality products were presented.

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ABSTRACT

Quality improvement of bio-paraffin by isomerization was studied in presence of fatty acid over Pt/SAPO-11 catalyst in order to produce second generation biogasoil. The reaction rates and activation energy of the isomerization having high importance in both reactor design and process control were determined. The increase of the fatty acid content of feedstock significantly decreased the rate of isomerization of bio-origin octadecane, but did not affect the activation energy being 143 ± 3 kJ/mol. Industrial application of the favourable results and the excellent quality properties of end products were also demonstrated.

1. Introduction

Bio-fuels and bio blending components have higher and higher importance both in Europe and all over the world, because of their environmental advantages [1,2].

Currently mainly methyl esters (biodiesels) are used as bio-components of diesel fuel that are produced by the transesterification of different vegetable oils and used frying oils generally with methanol. However during the production of biodiesels harmful wastes also form and the marketing of glycerine, as by-product is difficult [3–5]. Furthermore biodiesel products (mixtures of methyl esters) have a lot of performance disadvantages; for example their oxidation and heat stability is poor because of great number of olefininc bonds [3–5], the water content and the hydrolysis of ester bonds brings about corrosion problems [6,7] resulting in poor storage stability [3–5]. In addition because of the good conductivity corrosion may damage metallic parts; furthermore the solving nature may cause compatibility problems with plastic construction materials [8–10]. Due to these disadvantages the maintenance costs are higher, and the lifetime of the engine is shorter [9]. Because of the lower energy content the fuel consumption is higher [8,11]. The combustion characteristics differ from those of diesel fuels (ignition delay, adiabatic flame temperature, radiation heat loss, etc.), the NO_x emission is higher [8,9,11–13], the aldehyde emission is also higher [11]. In addition the cold filter plugging point is higher [9,12]; they have inadequate compatibility with lubricating oils [9], the after-treatment catalysts may be damaged by alkali and/or alkaline earth metals and phosphorus present in vegetable oils [6]; the production costs are also higher than for diesel fuels [5,14,15], etc. For these reasons car manufacturers recommend the blending concentration of the fatty acid methyl esters by 7.0 v/v% in the European Union in accordance with the EN 590:2009 standard. At the same time up to 2020 European Union prescribed to use 10% of bio origin component in fuels.

Because of the mentioned drawbacks and limits bio-fuels have to be produced, which have different chemical structure than biodiesel, and thus better performance characteristics. Such fuels are biogasoils produced from triglycerides by heterogeneous catalytic hydrogenation which consist mainly of normal and

* Corresponding author. Tel.: +36 88 624313; fax: +36 88 624520.
E-mail address: hancsokj@almos.uni-pannon.hu (J. Hancsók).

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iso-paraffins [16], accordingly they are more advantageous than biodiesels, excepted cold flow properties being important at low temperature e.g. under arctic conditions.

While during the production of fatty acid methyl esters a compromise has to be made between the use of highly olefinic (reactive) esters which guarantee good cold flow properties, and the highly saturated esters which ensure good cetane number and acceptable oxidation and storage stability [16–21]. On the other hand the normal and isoparaffin containing biogasoils can be produced from any type of triglycerides and fatty acids (e.g.: conventional and improved vegetable oils, used frying oils and fats, greases from leather and meat processing industry, brown grease of sewage farms, etc.) that can contribute to the further use of bio-fuels. From economical point of view those triglycerides are attractive which have low olefinic double bond content, since the lower the olefinic double bond content, the lower the hydrogen consumption during the hydrotreating [22].

Second generation bio-fuels – especially those ones which are produced by catalytic hydrogenation of triglycerides – have rather advantageous composition. They are practically free of sulfur and nitrogen, and have negligible olefin and aromatic content, but have high paraffin content thus performance properties are advantageous. As a consequence, regarding environmental and sanitary aspects the very harmful SO_x components are not formed during the application, the combustion results in low particulate emission, furthermore regarding the whole life cycle they have lower green house gas emission than fossil fuels [2].

However – as it was mentioned – these mixtures of high (>95%) normal paraffin content (mainly n-C_{12}–n-C_{20}) have unfavorable cold flow properties (the freezing point of normal paraffins is high, e.g. that of n-C_{18} is +28 °C) (Figs. 1 and 2) [20]. Accordingly the catalytic isomerization seems to be the most suitable final production step of biogasoils; wherein paraffin mixture having appropriate cold flow properties, freezing point and high cetane number can be produced with high yield using a suitable catalytic system (catalyst, reactor, process parameters, etc.) [16–21].

During the isomerization of these normal paraffin mixtures the cracking of the formed mono-branched and multi-branched paraffins takes place, as well. The cracking reactions take place by far lower degree in case of linear or mono-branched, than for multi-branched paraffins because of energetic reasons. The hydroisomerization and hydrocracking reactions, mainly their ratios are influenced by several factors like the composition, hydrogenation-dehydrogenation activity and the ratio of metallic/acidic sites of the applied catalyst, the processing parameters, furthermore the composition of the feedstock, etc. [23–25].

The isomerization of long chain paraffins, either as model compounds or fossil based hydrocarbon mixtures with at least 80–90% normal paraffin content was investigated in the last about 30 years

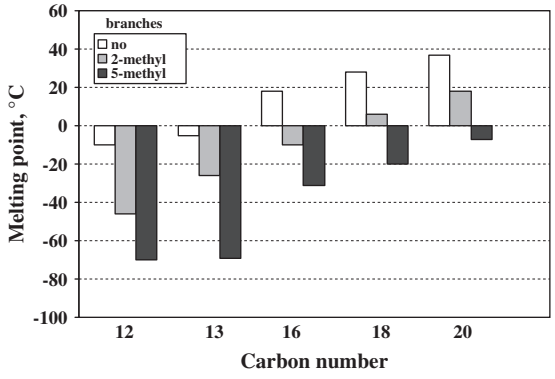

Fig. 1. Freezing point of the paraffins as a function of the carbon number [19].

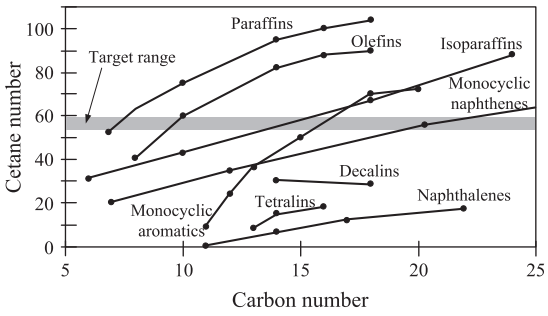

Fig. 2. Cetane number of different hydrocarbon groups as a function of the carbon number [19].

by several research teams in order to obtain low freezing point base oils or gas oils. The research comprised kinetic calculations beside the investigation of product composition, catalyst activity and selectivity [e.g. 26–30].

In order to produce bio-origin fuel blending components of C_{14}–C_{18} paraffins with suitable cold flow properties from natural triglycerides we carried out several isomerization test series, wherein mixtures of high isoparaffin content were produced with high yield, excellent cold flow properties and high cetane number. The influence of the composition of catalyst and feedstock was investigated on the isomerization of bio-paraffin mixture over different micro and mesoporous catalysts (noble metal containing HZSM-22, SAPO-11 and MCM-41) [16–20]. It has been found that partially hydrogenated natural triglycerides or different oxygen containing compounds (carboxyl acids, esters, aldehydes, etc.), furthermore other contaminants significantly decrease the degree of isomerization and the activity of the catalyst [16,19], and of course the quality of the end products.

Beyond the selection of the appropriate catalyst and the knowledge of the obtainable product yield and quality, the determination of reaction kinetic parameters has a priority having high importance in both reactor design and process control. In case of bio-paraffin mixtures such data are not available in the literature; especially the effects of oxygen containing compound on the isomerization reactions are unrevealed. Accordingly the aim of the present paper was the improvement of cold flow properties of fatty acid containing bio-paraffin mixtures over Pt/SAPO-11 catalyst, while the yield, product quality and reaction kinetic parameters (rate equation, rate constants and activation energies) were investigated in system-approach. Based on the obtained results the aim was to suggest an industrial implementation for the isomerization of bio-paraffin mixture in reactor systems used for isomerization of deeply hydrodesulfurized gas oils.

2. Experimental

2.1. Apparatus

In order to effectively achieve aims stated above the experiments were carried out in an apparatus containing a tubular down-flow reactor of 100 cm^3 effective volume. It is equipped with all the devices usual in heterogeneous catalytic industrial plants. Process parameters were controlled as accurately as in industry. The experiments were carried out in continuous operation with steady-state catalyst activity.

2.2. Process parameters

Reaction temperature (T = 260–360 °C) and the liquid hourly space velocity (LHSV = 0.5–5.0 h^{-1}) were varied. The total pressure