

Available online at website: https://journal.bcrec.id/index.php/bcrec

Bulletin of Chemical Reaction Engineering & Catalysis, 19 (3) 2024, 539-547



Research Article

Oligomerization of Fischer-Tropsch Olefins by Radical Initiation Method for Synthesizing Polyolefin Based Oils

Yash V. Kataria*, Vera P. Kashparova, Victor A. Klushin, Olga P. Papeta, Roman E. Yakovenko, Ivan N. Zubkov

Research Institute "Nanotechnologies and New Materials", Platov South-Russian State Polytechnic University (NPI), Novocherkassk 346428, Russia

Received: 27th August 2024; Revised: 16th October 2024; Accepted: 17th October 2024 Available online: 21th October 2024; Published regularly: October 2024



Abstract

In the present work we have investigated the oligomerization process of Fischer-Tropsch synthesis products – gasoline (C_{5} - C_{10}) and diesel (C_{11} - C_{18}) hydrocarbon fractions with a total olefin content (consisting mainly olefins with a branched isomeric chain) of 79.3 and 31.8 wt.%, respectively. Oligomerization was carried out by radical initiation method using azobisisobutyronitrile, benzoyl peroxide, dicumyl peroxide and methyl ethyl ketone peroxide (Butanox M-50) as initiators. It was established that the yield of the oligomerization process depending on the initiator used decreases in the following order: azobisisobutyronitrile > benzoyl peroxide > dicumyl peroxide > Butanox M-50. It was determined that when the oligomerization is carried out in polar solvents such as acetone and dichloromethane the yield of product increases by ~2.1 and ~1.7 times, respectively, while at the same time adding a non-polar solvent such as tetrachloromethane to the reaction mixture decreases the product yield by ~2.0 times. The optimal technological parameters for carrying out oligomerization process of synthetic gasoline and diesel fractions were determined: where azobisisobutyronitrile, content 0.5 wt.%., is used as an initiator, acetone as solvent, with reaction temperature of 200 °C, and duration of 12 hrs. under inert atmosphere. The product yield from the diesel fraction is 39.5 %, and from the synthetic gasoline fraction – 36.0 %. At the same time, in terms of characteristics, the oligomerization product of the diesel fraction showed properties similar to commercially available Base oil 3cSt (Group III), and the gasoline fraction showed properties on par with the commercially produced PAO-2 (Group IV).

Copyright © 2024 by Authors, Published by BCREC Publishing Group. This is an open access article under the CC BY-SA License (https://creativecommons.org/licenses/by-sa/4.0).

Keywords: Fischer-Tropsch synthesis; oligomerisation; olefins; polyolefin oils; radical polymerization; lubricant

How to Cite: Y. V. Kataria, V. P. Kashparova, V. A. Klushin, O. P. Papeta, R. E. Yakovenko, I. N. Zubkov (2024). Oligomerization of Fischer-Tropsch Olefins by Radical Initiation Method for Synthesizing Polyolefin Base Oils. Bulletin of Chemical Reaction Engineering & Catalysis, 19 (3), 539-547 (doi: 10.9767/bcrec.20205)

Permalink/DOI: https://doi.org/10.9767/bcrec.20205

1. Introduction

Poly-α-olefin (PAO) oils belong to group IV oils and by far remains the largest segment in the synthetic lubricant market. PAOs exhibit superior performance, such as improved viscosity index (VI), low pour point and volatility, high oxidative and thermal stability, and they retain sufficiently high viscosity at high temperatures and good flow properties at low temperature [1–3]. These types

of oils are fully compatible with mineral oils, which plays an important role in the production of synthetic and semi-synthetic lubricants [4]. Hydrotreated C₂₀-C₄₀ oligomer fractions represent the most valuable base stocks of high-quality lubricants. PAOs, based on their KV¹⁰⁰ (i.e. kinematic viscosity at 100 °C), are classified into several categories ranging from 2 to 100 cSt. For example, low-viscosity PAOs (for example, PAO-2, 4 and 6) are used in the production of high-performance synthetic automotive crankcase and transmission lubricants. In turn, high-viscosity

* Corresponding Author.

Email: katariayash1603@gmail.com (Yash V. Kataria)

PAO oils have a wide range of applications in various industries – automotive, aviation, space, etc. A significant increase in demand for both lowand high-viscosity PAO oils is expected in comparison with mineral-based base oils [5–7]. PAO oils are widely used as components of commercial oils obtained by compounding several base oils to improve volatility, high- or low-temperature viscosity, oxidative stability, etc. Due to the growing need for high-quality lubricants, an increase in the consumption of synthetic base oils is expected [8].

A wide range of catalytic routes and reaction conditions are employed to synthesize PAOs. Among them, Lewis acid catalyst, such as BF₃, is widely employed commercially for oligomerization of α-olefins for the production of low-viscosity oil (KV 100 = 2–10 cSt), suitable for low-temperature applications. Hanifpour et al. [9] have presented a very detailed review of all the currently employed catalyst systems oligomerization of α-olefins as well as their effect on the obtained PAOs. However, the work does not report about the use of radical initiation method for the oligomerization of α-olefins to PAOs. At the same time, there are very few works reported in literature as well on the use of radical initiation method for oligomerization of α -olefins [10].

The PAOs are usually synthesized from 1dodecene (C_{12}) and 1-decene (C_{10}) at the same time, research is currently underway to explore the possibility of using other monomers, starting from 1-hexene to 1-tetradecene [11,12]. At present, the main method for producing α-olefins is the oligomerization of ethylene [13,14]. Less common industrial methods for producing linear α-olefins include thermal cracking of n-paraffins and dehydration of alcohols. [15,16]. At the same time in recent years, olefins with different carbon chain lengths are obtained in the Fischer-Tropsch synthesis (FT) on zeolite-containing catalysts [17]. The FT synthesis of hydrocarbons from syngas is highly attractive way to convert carbon containing raw stocks (coal, natural or as sociated petroleum gas, biomass, etc.) into liquid hydrocarbons and is considered as an alternative method for producing raw materials, including unsaturated alkenes with different hydrocarbon chain lengths [18]. There are three major high-temperature FT refineries worldwide, and olefin oligomerization is a key refining technology in all of them [19,20]. The main reason for olefin oligomerization in a FT refinery is 2-fold, namely (i) to convert normally gaseous olefins to liquid products and (ii) to produce a fuel component (motor-gasoline, jet fuel, or diesel) that can be hydrogenated to reduce the overall olefin content of the fuel pool. However, these processes require a large number of additional steps which are not economically viable. In this regard, the possibility of using the gasoline (C_5 - C_{10}) and diesel (C_{11} - C_{18}) fraction of hydrocarbons to obtain base PAO oils is of both scientific and practical interest. To the best of our knowledge there is practically no information in the scientific literature about the possibility of producing PAOs using the FT synthesis products - a mixture of hydrocarbons containing, along with α -olefins, β - and γ -olefins, which are formed in significant quantities during the synthesis process, as well as about the properties of the resulting oils and possible areas of their application.

Previously, we had reported preparation of a bifunctional cobalt zeolite-containing catalyst [21], which is a composition based on an active metal oxide (catalyst for the synthesis of hydrocarbons) and zeolite, formed into granules using a binder. It was found [22] that using this catalyst, along gas circulation, it was possible to obtain a mixture of C_{5+} hydrocarbons, consisting of ~90% of gasoline and diesel (C_{11} - C_{18}) hydrocarbons with a total content of C_{5-} - C_{18} olefins up to 65.7 wt.%.

The aim of the present work is to explore the possibility of utilizing FT synthesis products gasoline (C₅-C₁₀) and diesel (C₁₁-C₁₈) for obtaining polyolefin base oils using radical initiation method. For the purpose of this work four different initiators azobisisobutyronitrile (AIBN), benzoyl peroxide, dicumyl peroxide and methyl ethyl ketone peroxide (Butanox M-50), have been studied. The reaction conditions as well as influence of different solvents like acetone, dichloromethane and carbon tetrachloride have been experimentally determined for optimizing the conditions. reaction The obtained oligomerized products have been characterized by the values of kinematic viscosity, pour point and density and based on the obtained results a has been drawn with comparison commercially available PAOs.

2. Materials and Methods

2.1 Methods for Studying Feedstock and Oligomerization Products

The quantification of gasoline and diesel obtained from the FT synthesis, as well as the oligomerization products, were determined using capillary gas-liquid chromatography-mass spectrometry (GC-MS) on an Agilent GC 7890A gas chromatograph with an MSD 5975C mass detector (Agilent Technologies, USA) and an HP-5MS column using helium as a carrier gas.

For studying the synthetic gasoline fraction the staring temperature was set at 30 °C and the sample was held for 5 mins using the oven program provided with Agilent GC 7890A gas chromatograph, further the temperature was increased by 5 °C/min up to 60 °C where sample

was held for 1 min, then by 10 °C/min to 70 °C where sample was held for 1 min and finally by 50 °C/min to 270 °C and the sample was held for 5 min.

For synthetic diesel fraction the staring temperature was set at 30 °C and the sample was held for 5 mins after which the temperature was increased by 5 °C/min up to 80 °C where sample was held for 1 min, then by 7 °C/min to 122 °C where sample was held for 1 min and finally by 10 °C/min to 292 °C and the sample was held for 3 min. The oligomerization products were studied at a starting temperature of 40 °C and the sample the sample was held for 0.5 mins after which the temperature was increased by 15 °C/min up to 220 °C where sample was held for 1 min and finally by 30 °C/min to 300 °C and the sample was held for 1 min and finally by 30 °C/min to 300 °C and the sample was held for 10 mins.

For determining low-temperature properties, the TPZ-LAB-12 automatic apparatus has been used, designed to determine the pour point in a small sample volume in accordance with ASTM D6749-02 "Standard Test Method for Pour Point of Petroleum Products (Automatic Air Pressure Method)." The determination of kinematic viscosity at temperatures of 40 and 100 °C has been carried out in accordance with ASTM D7042-16 [23].

2.2. Synthesis of hydrocarbon fractions

The hydrocarbon fractions were obtained by Fischer-Tropsch synthesis which was carried out in a tubular reactor (internal diameter 16 mm) with a stationary layer of 10 cm³ of bifunctional cobalt zeolite catalyst [21] (grain size 1.0-2.0 mm) at a pressure of 2.0 MPa, temperature 250 °C, H₂/CO ratio at the reactor inlet of 1.70, gas volumetric velocity of 1000 h-1 and circulation ratio of 0-16. Preliminary reduction of the catalyst was carried out for 1 hour in a flow of H₂ at a pressure of 0.1 MPa, a temperature of 400 °C and a gas volumetric velocity of 3000 h-1. When studying the influence of each individual technological parameter, fresh catalyst was loaded into the reactor. The resulting C₅₊ hydrocarbons at each value of the technological parameter were separated by distillation at atmospheric pressure, isolating fractions with a boiling point: up to 180 °C - C₅-C₁₀ hydrocarbons (gasoline), 180-final boiling point °C - C₁₁-C₁₈ hydrocarbons (diesel). The resulting fractions were designated as GAS-1 and DIS-1. respectively.

2.3. Reagents

For the purpose of this work the solvents acetone, carbon tetrachloride and dichloromethane we purchased from EKOS-1 (Russian Federation) and are used without any further purification. The initiators for radical

oligomerization process AIBN, benzoyl peroxide, dicumyl peroxide and Butanox M-50, were purchased from Sigma Aldrich (99 % purity).

2.4. Oligomerization

The oligomerization of synthetic hydrocarbon fractions enriched with olefins is carried out in an autoclave (PTFE-0300) with constant stirring and a magnetic stirrer speed of 550 rpm to ensure effective mass transfer in the system at a temperature of 200 °C for 3-36 hours. The mass content of the initiator is varied in the range of 0.1-1.5 % (with respect to olefin content in the feed fraction). The amount of loaded synthetic hydrocarbon fraction for each experiment consisted 20 mL, the volume of solvent (acetone, CH₂Cl₂, CCl₄) is varied from 0 to 50 mL. The process was carried out in an inert environment the autoclave was previously evacuated and purged with argon; this treatment was carried out three times to completely remove air. A typical experiment consists of loading 20 mL of synthetic hydrocarbon fraction into a pre-evacuated autoclave with an AIBN initiator of 0.5 wt.% (with respect to olefin content in the feed fraction), dissolved in 40 mL of acetone, in an inert environment with constant stirring of 550 rpm min and temperature 200 °C for 12 hours. The resulting mixture after oligomerization was subjected to separation by fractionation at atmospheric pressure. The yield was determined as the ratio of the mass of the bottom residue after distillation (in the case of a diesel fraction above a temperature of 305 °C, a gasoline fraction above a temperature of 220 °C) to the weight of the original loaded raw material.

3. Results and Discussion

3.1. Characteristics of The Raw Material

The density of sample DIS-1 is 770 kg/m³, and sample GAS-1 is 714 kg/m³, respectively (Table 1). The lower densities of synthetic diesel and gasoline fractions compared to similar fractions obtained from petroleum feedstock are due to the absence of aromatic hydrocarbons in their composition. The composition of both fractions is represented by n- and iso-alkanes, alkenes and branched alkenes. While the alkenes are linear unsaturated hydrocarbons that involve a change in the position of the double bond in the structure of the hydrocarbon chain, the branched-alkenes are alkenes that have isomerized hydrocarbon chain (by analogy with isomers of n-alkanes (isoalkanes). isomers of alkenes that have isomerization of the chain are labeled as branched-alkenes). The total alkene content is 31.8 and 79.3 wt.%, respectively, the predominant amount of which are alkenes with branched isomeric chains. It can be noted that the content

of iso-structure hydrocarbons is slightly higher in the GAS-1 sample (iso/n index is 1.79 versus iso/n equal to 1.38 in the DIS-1 sample). The pour point of sample DIS-1 is -17 °C, sample GAS-1 is below 65 °C (it is not possible to determine the exact value due to the fact that the pour point of sample GAS-1 is below the threshold value of the operating temperature range of the device).

Sample DIS-1 consists predominantly of a fraction of hydrocarbons with a chain length of C_{11} - C_{18} (~75 wt.%) and a small amount of a fraction of C_5 - C_{10} and C_{19+} (Figure 1a). Sample GAS-1 consists predominantly of a fraction of hydrocarbons with a chain length of C_5 - C_{10} (~89 wt.%) and C_{11+} (Figure 1b). The presence of hydrocarbons with a different hydrocarbon chain length in each of the samples is due to the method of obtaining the fractions, since simple distillation at atmospheric pressure, which is used in laboratory conditions, cannot clearly separate complex multicomponent mixtures.

3.2. Effect of Reaction Duration

Preliminary studies to determine the optimal duration of the oligomerization process were carried out at a temperature of 200 °C, an initiator content of 0.1 wt. % (AIBN, benzoyl peroxide, dicumyl peroxide, Butanox M-50) and using sample DIS-1 as a feedstock (Figure 2).

In general, the formation of oligomerization product increases with an increase in the reaction time. However, a significant increase in the yield can be noticed in the first 12 h. of reaction after which a further increase in the reaction time shows a minor change in the reaction yield. From the experiments it is established that when the AIBN is deployed for radical initiation a maximum formation of oligomerization product of ~14 % can be observed, at the same time with Butanox M-50 a yield of just 3.2 % can be obtained when the oligomerization is carried out for 12 h. (see Figure 2). Benzoyl peroxide and dicumyl

Table 1. Composition and properties of synthetic hydrocarbon fractions

Sample	Composition	Content, wt. %		Ratio			
			ρ, kg/m³	branched alkenes/alkenes	o/pa	iso/n ^b	T _{pour.} , °C ^c
DIS-1	n-alkanes	39.1		10.0	0.47	1.38	-17
	<i>iso</i> -alkanes	29.1					
	alkenes	2.9	770				
	branched-alkenes	28.9					
	Total	100.0					
GAS-1	n-alkanes	13.6		2.6	3.83	1.79	141
	<i>iso</i> -alkanes	7.1					
	alkenes	22.2	714				less than -65
	branched-alkenes	57.1					-69
	Total	100.0					

^a ratio of alkenes to alkanes (olefins to paraffins);

^c the temperature below which the liquid loses its flow characteristics

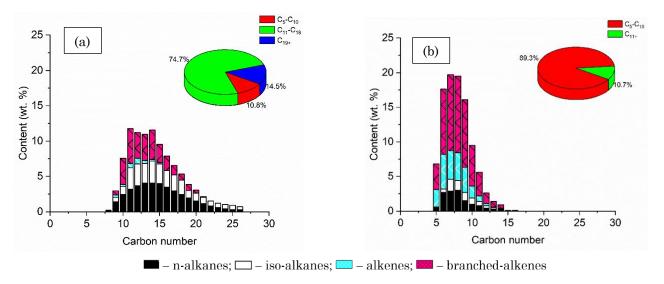


Figure 1. Molecular weight distribution of synthetic hydrocarbon fractions DIS-1 (a) and GAS-1 (b)

^b ratio of hydrocarbons of iso-structures to hydrocarbons of normal structure;

peroxide gave reaction yields of around 12 % and 8 %, respectively.

3.3. Effect of Initiator Loading

At the same time, it is also very important to determine the optimal amount of initiator loading for the oligomerization of DIS-1 feedstock. For this we conducted experiments with varying initiator loadings from 0.1 to 1.5 wt. % with respect to olefin content in the feed fraction at a temperature of $200~^{\circ}\mathrm{C}$ for $12~\mathrm{h}$.

As it can be seen from Figure 3 the initiator loading indeed shows a significant influence on the oligomerization of synthetic diesel fraction. For all the initiators it is found that with an increase in their loading from 0.1 % to 0.5 % an increase in the product yield is observed. When using AIBN and benzoyl peroxide as initiators the product yield increases by ~1.4 times and in the case of dicumyl peroxide and Butanox M-50 an increase of ~2.0 times in observed. The half-life temperature of the initiator increases in the order AIBN> benzyl peroxide> dicumyl peroxide> Butanox M-50, which in turn, explains the higher activity of AIBN and benzyl peroxide compared to the other initiators, that is, they begin to initiate the process faster [24]. One the other hand, a further increase in the initiator loading does not increase the product yield, in fact, a decrease of ~1.1 times with all the initiators is observed. This can be explained by fact that with an increase in the initiator content increases the amount of active radical centers which up to a certain concentration increase the product yield, however with an excess of radical formation the probability of oligomerization chains breaking increases resulting a large number of short-chain molecules (<C₂₀), that get separated during the distillation process, which, in turn, reduces the yield of products.

The authors of [10], when studying the radical oligomerization of 1-octene, as a model compound, at a temperature of 150 °C for 16 hours and using di-tert-butyl peroxide as an initiator, based on GC-MS data, recorded a maximum yield of 12.1 %. In this work, using AIBN and benzoyl peroxide, a yield of \sim 17-19 % is achieved, dicumyl peroxide \sim 12.5 %, and Butanox M-50 \sim 7.5 %. While the product yield increases and is in fact more than what is reported in the literature [10], it is however still less.

3.4. Effect of Solvent

The influence of solvents on the process of oligomerization of individual monomers has been studied quite well [10]. However, the features of changes in the yield of the oligomerization process of multicomponent mixtures with different monomers remain unclear. Therefore, in the present work we decided to carry out of the oligomerization of sample DIS-1 in polar (acetone, CH₂Cl₂) and non-polar (CCl₄) solvents with an initiator content of 0.5 wt.%, temperature 200 °C for 12 hrs. with constant stirring for all selected initiators.

As it can be seen from Figure 4 addition of polar solvent to the reaction mixture significantly product When increases the yield. oligomerization reaction is carried out in acetone the product yield increases by ~2.1 times, at the same time when dichloromethane is used as solvent the product yield increases by ~ 1.7 times. In contrast when the reaction is carried out in a non-polar solvent such as carbon tetrachloride a drop in the product yield of ~2.0 times. The higher solubility of reaction elements in polar solvents leads to rapid polymer formation, which increases free radical diffusion in the reaction mixture and induces the termination reaction. Hence, a polar

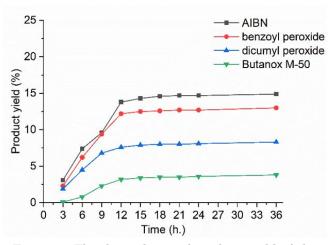


Figure 2. The dependence of product yield of the DIS-1 feedstock on the reaction time of oligomerization process.

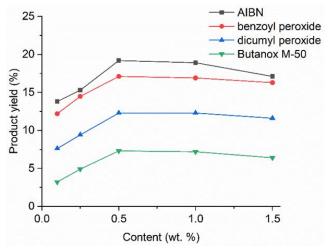


Figure 3. Influence of initiator loading on the product yield of DIS-1 feedstock

solvent would have a more rapid chain termination rate of macroradicals than a nonpolar solvent [25]. The drop in the product yield is further conformed by the work of Cowley [10] where the influence of non-polar solvent such as benzene on the product yield was studied. The maximum product yield for sample DIS-1 (39.5 %) is obtained when AIBN is used as an initiator (0.5 wt.%), acetone as solvent (40 mL), a temperature 200 °C and reaction time of 12 hrs.

In turn, the use of different feedstocks, for example, the C_5 - C_{10} fraction enriched in olefins (sample GAS-1), can help obtain products with different properties. As a result, studies of the oligomerization process of the GAS-1 sample were also carried out under the same conditions giving a product yield of 36 %.

3.5. Composition and Properties of Oligomerization Products

Base on the GC-MS analysis it is found that the oligomerization product DIS-1L (Figure 5a) consist mainly of C_{19+} hydrocarbons having normal and branched structure. The C_{25+} hydrocarbons content is ~ 76 %, which indicates the formation of dimers and trimers of C_{13} - C_{18} hydrocarbons as a result of radical

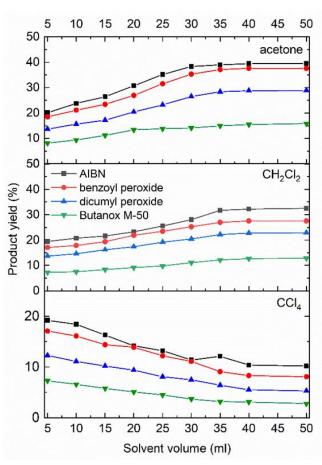


Figure 4. Product yield of the DIS-1 sample oligomerization process depending on the nature of the solvent

oligomerization of unsaturated hydrocarbons found in the diesel fraction. The content of branched C_{19+} hydrocarbons is ~67 %, which can be explained by the presence of large amounts of branched alkenes in the feedstock.

The product GAS-1L (Figure 5b) also consists mainly of C₁₉₊ hydrocarbons ~86 wt.%. At the same time the content of C_{25+} hydrocarbons are ~ 59 %, which indicates the formation of trimers and tetramers of C₈-C₁₀ hydrocarbon as a result of radical oligomerization of gasoline fraction. The content of branched C₁₉₊ hydrocarbons is ~80 %, which is due to the presence of significantly high amounts of branched alkenes in the feedstock. The presence of the C₁₄-C₁₈ hydrocarbon fraction in the oligomerization products is the result of incomplete distillation of the low-boiling fraction due to the close boiling temperatures of the fractions. The ratio of isomeric compounds to normal hydrocarbons (iso/n) for oligomerization products of samples DIS-1L and GAS-1L is 2.0 and 3.6, respectively.

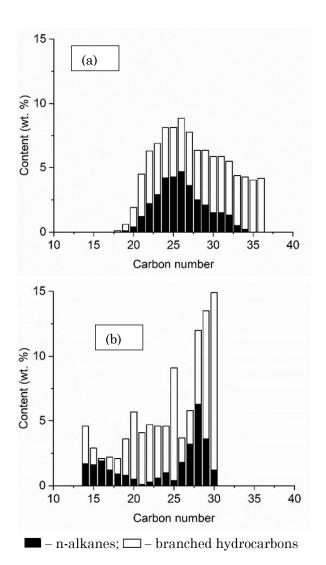


Figure 5. Molecular mass distribution of oligomerization products DIS-1L (a) and GAS-1L (b) $\,$

One of the main criteria for classifying oils is the value of kinematic viscosity at a temperature of 100 °C (KV100) and the viscosity index (VI). As a general rule, the presence of a long linear chain as a branch or main chain enhances the VI of synthetic oils, however, it is detrimental to low pour point. In other words, highly branched structures improve low-temperature characteristics (lower pour point), but, excessive short-chain branching reduce the VI value [26]. effect is clearly visible from characteristics of synthesized DIS-1L and GAS-1L oils. This effect is clearly visible in the obtained oils DIS-1L and GAS-1L (Table 2).

As it can be seen from the Table 2 the DIS-1L has a KV¹⁰⁰ of 3.44 cSt and VI of 146 which is very similar commercially the available SpectraSyn TM MaX 3.5 [27] (Group IV) synthetic oil produced by ExxonMobil. However, the DIS-1L has a very high pour point of -9 °C compared to the commercially available SpectraSyn™ MaX 3.5 (Group IV) which has a pour point of <-78 °C. This can be explained by the presence of significant amounts paraffins (n-alkanes) in the synthesized DIS-1L (~ 33 %, see Figure 5) which results in increase of pour point. At the same time, we decided to compare the properties of DIS-1L with commercially available Base oil 3cSt (Group III) [28] traded by Buoyancy Impex, which contain no chemically produced components and have a high amount of saturates with a KV100 of 3.26 cSt and VI of 116 which is less than the synthesized DIS-1L, as well as the pour point of -25 °C which is bit lower than the synthesized one. While the GAS-1L, oligomerization product of synthetic gasoline fraction has KV100 of 1.6 cSt and a pour point of -50 °C which are very similar to the commercially available group IV PAO-2 oils (see Table 2). The densities of the synthesized DIS-1L and GAS-1L oils are slightly lower in comparison to the commercially available group III and IV base oils [28-30]. One of the possible ways to improve the pour point characteristics is by passing the oligomerization products DIS-1L and GAS-1L through of deparaffinization/ stage isodewaxing to reduce the paraffin amount. In order to study the effect of oligomerization on

synthetic diesel and gasoline fractions, we decided to measure their pour point before loading in the and after distilling autoclave from oligomerization products. In the case of synthetic gasoline, no significant change in the pour point is observed, at the same time, for the synthetic diesel fraction the pour point decreases by ~2 times from -17 °C to -33 °C. This can be explained by the improved iso/n ratio for the distilled synthetic diesel fraction, because of formation of paraffins in the oligomerization product DIS-1L. This is confirmed by the GC-MS analysis of distilled synthetic diesel fraction, which has an iso/n ratio of 2.54 in comparison with the 1.45 (see Table 1).

4. Conclusions

In the present work for the first time the process of radical-initiated oligomerization of synthetic gasoline and diesel hydrocarbon fractions, enriched predominantly with branched olefins, obtained in the Fischer-Tropsch synthesis is reported. The fundamental possibility of obtaining poly olefin base oils using olefins obtained by the Fischer-Tropsch synthesis has been demonstrated. The optimal technological parameters for the oligomerization process of synthetic gasoline and diesel fractions were determined: initiator AIBN, initiator content 0.5 wt.%, acetone solvent, temperature 200 °C and reaction time of 12 hrs. In this case, the yield of the oligomerization process of the diesel fraction is 39.5 %, of the gasoline fraction -36.0 %. Kinematic viscosity at a temperature of 100 °C, viscosity index, density, and pour point of the obtained DIS-1L and GAS-1L samples were determined. Analysis of the properties of the DIS-1 L sample showed that, despite the fact that they are inferior in properties to Base oil 3cSt (Group III), they are very close. The properties of the GAS-1L sample are as close as possible to the properties of commercially produced PAO-2 (Group IV).

Table 2. Characteristics of synthesized and commercially available Group III and IV base oils

Sample	$\mathrm{KV}^{100},\mathrm{cSt}$	VI	ρ , kg/m ³	$T_{\mathrm{pour.}}$, $^{\circ}\mathrm{C}$
DIS-1L	3.44	146	802	-9
GAS-1L	1.6	-	743	-50
SpectraSyn™ MaX 3.5 (Group IV) [27]	3.55	129	817	Less than -78
Base oil 3cSt (Group III) [28]	3.26	116	830	-25
tatneft-nknkh-oil (Group IV) [29]	1.7 - 2.0	-	780-815	-60
TAIF lubricants (Group IV) [30]	1.75	-	797	-75

Acknowledgment

The research has been carried out with the financial support of the Russian Science Foundation Grant No. 23-23-00466 using the equipment of the Center for Shared Use "Nanotechnologies" of the Platov Southern Russian State Polytechnic University (NPI).

CRediT Author Statement

Yash V. Kataria: Writting Draft Preparation, Resources; Vera P. Kashparova: Methodology, Formal Analysis; Victor A. Klushin: Methodology, Formal Analysis, Data Curation, Writing - Review & Editing; Olga P. Papeta: Methodology, Investigation, Visualization; Roman E. Yakovenko: Writing, Review and Editing; Ivan N. Zubkov: Conceptualization, Supervision, Data Curation. All authors have read and agreed to the published version of the manuscript.

References

- [1] Benda, R., Bullen, J., Plomer, A. (1996). Synthetics basics: Polyalphaolefins – base fluids for high-performance lubricants. *Journal of Synthetic Lubrication*, 13(1), 41-57. DOI: 10.1002/jsl.3000130105.
- [2] Wu, M.M., Ho, S.C., Forbus, T.R. (2006). Synthetic lubricant base stock processes and products. Practical Advances in Petroleum Processing, 553-577.
- [3] Ray, S., Rao, P.V., Choudary, N.V. (2012). Polyα-olefin-based synthetic lubricants: a short review on various synthetic routes. *Lubrication Science*, 24(1), 23-44. DOI: 10.1002/ls.166.
- [4] Wu, M.M., Ho, S.C., Luo, S. (2017). Synthetic lubricant base stock. Springer Handbook of Petroleum Technology, 1043-1061. DOI: 10.1007/978-3-319-49347-3_35.
- [5] Hogg, J.M., Ferrer-Ugalde, A., Coleman, F., Swadźba-Kwaśny, M. (2019). Borenium ionic liquids as alternative to BF3 in polyalphaolefins (PAOs) synthesis. ACS Sustainable Chemistry & Engineering, 7(17), 15044-15052. DOI: 10.1021/acssuschemeng.9b03621.
- [6] Coffin, P.S., Lindsay, C.M., Mills, A.J., Lindenkamp, H., Fuhrmann, J. (1990). The application of synthetic fluids to automotive lubricant development: trends today and tomorrow. *Journal of Synthetic Lubrication*, 7(2), 123-143. DOI: 10.1002/jsl.3000070204.
- [7] Rudnick, L.R. (Ed.). (2020). Synthetics, Mineral Oils, and Bio-Based Lubricants: Chemistry and Technology. CRC press.
- [8] Hsu, C.S., Robinson, P.R., Hsu, C.S., Robinson, P.R. (2019). Lubricant processes and synthetic lubricants. *Petroleum Science and Technology*, 253-285. DOI: 10.1007/978-3-030-16275-7_13.

- [9] Hanifpour, A., Bahri-Laleh, N., Mohebbi, A., Nekoomanesh-Haghighi, M. (2022). Oligomerization of higher α-olefins to poly (α-olefins). *Iranian Polymer Journal*, 1-20. DOI: 10.1007/s13726-021-01011-x.
- [10] Cowley, M. (2007). Oligomerisation of alkenes by radical initiation. *Organic Process Research & Development*, 11(2), 286-288. DOI: 10.1021/op060253y.
- [11] Jiang, H., Yu, K. (2017). Catalytic polymerization of 1-decene using a siliconbridged metallocene system. *Petroleum Science* and *Technology*, 35(14), 1451-1456. DOI: 10.1080/10916466.2017.1344706.
- [12] Nifant'ev, I.E., Vinogradov, A.A., Vinogradov, A.A., Sedov, I.V., Dorokhov, V.G., Lyadov, A.S., & Ivchenko, P.V. (2018). Structurally uniform 1-hexene, 1-octene, and 1-decene oligomers: Zirconocene/MAO-catalyzed preparation, characterization, and prospects of their use as low-viscosity low-temperature oil base stocks. Applied Catalysis A: General, 549, 40-50. DOI: 10.1016/j.apcata.2017.09.016.
- [13] Keim, W. (2013). Oligomerization of ethylene to α-olefins: discovery and development of the shell higher olefin process (SHOP). Angewandte Chemie International Edition, 52(48), 12492-12496. DOI: 10.1002/anie.201305308.
- [14] Naji-Rad, E., Gimferrer, M., Bahri-Laleh, N., Nekoomanesh-Haghighi, M., Jamjah, R., Poater, A. (2018). Exploring basic components effect on the catalytic efficiency of Chevron-Phillips catalyst in ethylene trimerization. *Catalysts*, 8(6), 224. DOI: 10.3390/catal8060224.
- [15] Bursian, N.R., Kogan, S.B. (1989). Catalytic conversion of paraffinic hydrocarbons into isoparaffins and olefins. Russian Chemical Reviews, 58(3), 272. DOI: 10.1070/RC1989v058n03ABEH003439.
- [16] Dalin, M.A. (1984). Higher Olefins (Production and Application). Khimiya, Leningrad.
- [17] Pan, X., Jiao, F., Miao, D., Bao, X. (2021). Oxide–zeolite-based composite catalyst concept that enables syngas chemistry beyond Fischer–Tropsch synthesis. *Chemical Reviews*, 121(11), 6588-6609. DOI: 10.1021/acs.chemrev.0c01012.
- [18] Alsudani, F.T., Saeed, A.N., Ali, N.S., Majdi, H.S., Salih, H.G., Albayati, T.M., Cata Saady, N.M., Shakor, Z.M. (2023). Fisher–Tropsch Synthesis for Conversion of Methane into Liquid Hydrocarbons through Gas-to-Liquids (GTL) Process: A Review. Methane, 2(1), 24-43. DOI: 10.3390/methane2010002.
- [19] Marriott, J.N. (1986). Sasol process technologythe challenge of synfuels from coal. *Chemsa*; (South Africa), 12(8).
- [20] de Klerk, A. (2006). Oligomerization of Fischer– Tropsch olefins to distillates over amorphous silica– alumina. *Energy & Fuels*, 20(5), 1799-1805. DOI: 10.1021/ef060169j.

- [21] Yakovenko, R.E., Savost'yanov, A.P., Narochniy, G.B., Soromotin, V.N., Zubkov, I.N., Papeta, O.P., Svetogorov, R.D., Mitchenko, S.A. (2020). Preliminary evaluation of a commercially viable Co-based hybrid catalyst system in Fischer-Tropsch synthesis combined with hydroprocessing. Catalysis& Science 10(22), Technology, 7613-7629. DOI: 10.1039/D0CY00975J.
- [22] Zubkov, I.N., Denisov, O.D., Timokhina, M.A., Savost'yanov, A.P., Yakovenko, R.E. (2024). Study of the influence of the gas circulation ratio on the production of C5–C18 alkenes in the Fischer–Tropsch synthesis. *Kataliz v promyshlennosti*. 24, 34-42. (in Russian). DOI: 10.18412/1816-0387-2024-2-34-42.
- [23] ASTM D7042-21a Standard Test Method for Dynamic Viscosity and Density of Liquids by Stabinger Viscometer (and the Calculation of Kinematic Viscosity) (2021)
- [24] Matyjaszewski, K., & Davis, T. P. (2002). Handbook of Radical Polymerization. New York: Wiley-Interscience.
- [25] Rana, M.M., Rajeev, A., Natale, G., De la Hoz Siegler, H. (2021). Effects of synthesis-solvent polarity on the physicochemical and rheological properties of poly (Nisopropylacrylamide)(PNIPAm) hydrogels. *Journal of Materials Research and Technology*, 13, 769-786. DOI: 10.1016/j.jmrt.2021.05.009.

- [26] Shao, H., Gu, X., Wang, R., Wang, X., Jiang, T., Guo, X. (2020). Preparation of lubricant base stocks with high viscosity index through 1-decene oligomerization catalyzed by alkylaluminum chloride promoted by metal chloride. *Energy & Fuels*, 34(2), 2214-2220. DOI: 10.1021/acs.energyfuels.9b04104.
- [27] ExxonMobil SpectraSyn™ MaX 3.5 (1 August 2024). Citing Internet sources URL https://www.exxonmobilchemical.com.
- [28] Base oil 3cSt (Group III) (1 August 2024). Citing Internet sources URL https://buoyancyimpex.com.
- [29] Tatneft (1 August 2024). Citing Internet sources URL https://tatneft-maslo.narod.ru/files/production.html.
- [30] Taif-lubricants (1 August 2024). Citing Internet sources URL: https://taif-lubricants.ru/pao/pao/