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RESEARCH ARTICLE OPEN ACCESS

Synthesis of Gasoline and Kerosene by Heterogeneously Catalyzed (Co-)Oligomerization of Ethylene, Propylene, and Iso-Butylene

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Received: 20 October 2025 | **Revised:** 22 December 2025 | **Accepted:** 13 January 2026

Keywords: gasoline | heterogeneous catalysis | kerosene | methanol | olefins | oligomerization | sustainable aviation fuels (SAF)

ABSTRACT

The heterogeneously catalyzed co-oligomerization of ethylene, propylene, and iso-butylene was studied focusing on the production of gasoline and kerosene. Silica-alumina catalysts were employed with and without nickel loading. Initially, the homo-oligomerization of iso-butylene was studied employing a series of catalysts and varying reaction conditions. Due to the high reactivity of iso-butylene, conversion was almost quantitative and selectivities to kerosene reached 96% while selectivities to gasoline reached 83%. Subsequently, co-oligomerization of iso-butylene with ethylene and propylene was investigated. Employing nickel-loaded silica-alumina catalysts, all olefin species can be converted, despite the very different reactivity. Selectivities to kerosene and gasoline were up to 92% and 83%, respectively. It is shown that iso-butylene can be easily separated from such olefin mixtures by oligomerization, due to its much higher reactivity compared to propylene and ethylene. A long-term run lasting for 196 h showed continuous deactivation of the catalyst regarding the conversion of ethylene and propylene, whereas conversion of iso-butylene remained close to 100%. As a result, conversion of iso-butylene dominates and molecular branching increases, as indicated by the isoindex. It is shown that the catalyst can be easily reactivated by heating and catalytic performance can be fully restored.

1 | Introduction

Renewable fuels offer the opportunity to achieve carbon neutrality for existing fleets across the whole transportation sector. Liquid fuels will still be necessary in the future, especially in the aviation sector, where electrification is a challenge due to the lower energy density of batteries compared to liquid fuels [1, 2]. In aviation, the cold flow properties of kerosene play an important role, since at cruising altitude the fuel must not freeze. This can be prevented by a high degree of branching on molecular level. In the case of gasoline, a high degree of branching is also advantageous, as this can improve the knocking resistance. The threefold branched octanes are characterized by a research octane number (RON) of 100, an indicator of high knocking resistance [3] and the RON decreases significantly with decreasing molecular branching. Consequently, for kerosene as well as gasoline applications, highly branched molecules are beneficial with respect to fuel properties.

A viable pathway for the synthesis of branched hydrocarbons is olefin oligomerization. By coupling light olefins (C_{2-4}) to oligomers with carbon chain lengths from C_5 to approximately C_{16}, it allows for the production of gasoline and kerosene with high yields. Using iso-butylene as feedstock, oligomerization and subsequent hydrogenation yields highly branched fuels. Its hydrogenated dimer, the threefold branched iso-octane (C_8), can be applied as a gasoline blending component, just like the trimer iso-dodecane (C_{12}). Both molecules exhibit a RON of 100. In addition, iso-dodecane is suitable as a kerosene blendstock, as is the tetramer iso-hexadecane (C_{16}). Consequently, high-quality fuels for gasoline and kerosene applications can be produced from iso-butylene through the targeted synthesis of these three molecules.

Commercially, Neste has already demonstrated the conversion of iso-butylene to iso-octane in their NEXOCTANE process [4]. In this process, high selectivities to the dimer iso-octene are achieved on acidic ion exchange resins and the olefin is subsequently hydrogenated [5]. UOP invented the InAlk process using solid phosphoric acid as catalyst to convert olefins [6, 7]. Next to the oligomerization, GEVO initially synthesizes iso-butylene via the dehydration of iso-butanol obtained by fermentation [8]. Afterwards, iso-butylene is oligomerized to the main product iso-dodecene, together with the byproducts iso-octene and iso-hexadecene. The iso-butylene oligomerization was developed in cooperation with IFP Axens, which has several oligomerization processes in its portfolio, such as the homogeneously catalyzed processes Dimersol G and X, and the heterogeneously catalyzed processes Polynaphtha and Selectopol [9, 10]. The latter is explicitly recommended for iso-butylene oligomerization to high-octane gasoline components [9]. Heterogeneous catalysts have proven to be advantageous compared to homogeneous catalysts especially due to facile separation of the reaction systems coming along with economic benefits [11].

In general, a variety of different materials can be used as catalysts for the oligomerization of iso-butylene. Several investigations have been carried out with various ion exchange resins like Amberlyst or Dowex [12–16]. Additionally, zeolites [17–22], metal-organic frameworks [23], acid-treated clays [24], heteropoly-acids [25], and aluminas [26] have been studied. Another approach is the use of supported catalysts and, for example, supported chloroaluminate [27, 28], iron [29], or nickel [26, 30–39] species have been investigated. In this context, catalysts based on silica-alumina materials with and without nickel loading showed outstanding performance in oligomerization reactions of ethylene, propylene, and 1-butylene, especially with regard to fuel selectivity [40, 41]. Moreover, it has been shown that the presence of mesopores is advantageous in terms of reduced deactivation of the catalyst by deposits of higher oligomers. In addition, acidity of the catalysts, which is relevant for the degree of oligomerization, can be specifically adjusted by varying the ratio of silica to alumina. A low number of Brønsted sites limits conversion but has proven to be advantageous for the long-term stability of the catalysts. Therefore, and in order to find the most suitable catalysts, mesoporous silica-alumina materials with different densities of Brønsted sites and different nickel loadings were used and compared in this study.

In contrast to the homo-oligomerization of iso-butylene, its co-oligomerization with other olefins has been sparsely studied. However, this is also relevant since light olefin mixtures like those from Methanol-to-Olefins (MtO) processes can contain substantial amounts of iso-butylene [42, 43]. In recent work, the co-oligomerization of 1-butylene with ethylene and propylene was addressed [44] and the present study aims for supplementing the previous results by replacing 1-butylene in the olefin mixture with iso-butylene. As already mentioned above, a different reactivity and an increased molecular branching can be expected. Thus, a focus of this work is on the influence of catalysts and reaction conditions on the properties and quality of the resulting fuels. As far as kerosene production is concerned, Sustainable Aviation Fuels (SAF) can be obtained via co-oligomerization, provided that the olefins are obtained sustainably from renewable resources [45–52].

2 | Experimental Section

Mesoporous silica-alumina materials from Sasol were used as oligomerization catalysts, which are commercially available under the trade name SIRALOX. There are various specifications that differ in the ratio of SiO_2 to Al_2O_3. Blank silica-aluminas as well as nickel-loaded systems were used and their labelling indicates the proportions of SiO_2, Al_2O_3 and nickel in the material. For example, 20/2Ni consists of approximately 20% SiO_2, 80% Al_2O_3, and the nickel loading is 2 wt%. For the preparation of the nickel-loaded catalysts, SIRALOX was first calcined at 550°C for 8 h. Then, nickel was loaded using the incipient wetness impregnation method. A nickel salt solution of $Ni(NO_3)_2 \cdot 6\,H_2O$ (99.9% from ABCR) was prepared with distilled water and added to the support. After drying at 50°C and subsequent calcination at 550°C, a particle size of 250 to 500 µm was adjusted by sieving [40].

Silica-alumina compositions (*Si*/*Al*) of the catalysts were measured by ICP-OES while surface properties such as specific surface area (S_{BET}), pore diameter (d_{Pore}), and the specific pore volume (V_{Pore}) were determined by nitrogen physisorption. Acidity of the catalysts was measured by NH_3-TPD and FTIR spectroscopy. Pyridine was used as a probe molecule and by this, Lewis and Brønsted acid sites could be distinguished and the density of Brønsted acid sites ($N_{\mathrm{Brønsted\ sites}}$) was quantified. Some of the most important properties are summarized in Table 1 and a more detailed characterization of the catalysts can be found in previously published studies [40, 41, 44].

The oligomerization experiments were conducted employing a continuously operating fixed-bed reactor. In each experiment, 5 g of fresh catalyst were used, without any activation. After the inlet section consisting of silicon carbide (SiC), a mixture of the catalyst and SiC was placed in the middle of the reactor. To enable an isothermal operation of the reactor, the catalyst was mixed with the tenfold volume of silicon carbide. Regarding the olefin feed, ethylene (99.9%, Air Liquide), propylene (99.5%, Air Liquide), and iso-butylene (99.5%, Air Liquide) were utilized in a ratio of 40:40:20 vol%. Argon (99.999%, Air Liquide) was applied as an inert gas to serve as a reference for online gas analysis. Unless otherwise stated, all results refer to a time on stream (ToS) of 4 h. Further details on the plant design and the experiments were previously reported [40, 41, 44].

The analysis of gaseous products was carried out online using a HP 5890 gas chromatograph equipped with a Rt-Alumina BOND/Na_2SO_4 column. The liquid products were quantified offline using an Agilent GC 6890 with a DB-1 column. Detailed determination of specific molecules up to a chain length of C_8 was performed after the elimination of stereoisomers by

TABLE 1 | Surface properties of Siralox 20 (20/0Ni), Siralox 40 (40/0Ni), Siralox 70 (70/0Ni), and the nickel-loaded catalysts 20/2Ni, 40/2Ni, and 70/2Ni.

Catalyst	Si/Al (mol/mol)	S_{BET} (m^2/g)	d_{Pore} (nm)	V_{Pore} (ml/g)	$N_{Brønsted\ sites}$ (μmol/g)
20/0Ni	0.2	495	7.3	1.26	26.4
20/2Ni	0.2	414	7.8	1.02	21.5
40/0Ni	0.6	455	9.2	1.57	46.8
40/2Ni	0.6	373	7.1	1.14	35.4
70/0Ni	1.6	331	11.2	1.44	33.5
70/2Ni	1.4	286	8.3	0.93	27.5

hydrogenation of the fuels according to Heveling et al. [53]. For hydrocarbons with a chain length of C_9 and above, a detailed differentiation of isomers was not possible due to the rapidly growing number of different isomers. It should be mentioned that the assignment of GC signals to carbon chain lengths was carried out using simulated distillation. This means that highly branched molecules can fall into the range of lower chain lengths and obscure the actual product distribution. This occurs, for example, in the case of the iso-octenes and iso-dodecenes, respectively, which are assigned to the C_7, and C_{10} and C_{11} fractions, respectively. For iso-butylene homo-oligomerization, the correction of the carbon chain lengths to C_8 and C_{12} is straightforward due to the absence of side reactions such as metathesis. However, for the co-oligomerization of iso-butylene with propylene and ethylene, the differentiation is no longer possible due to the increased number of possible oligomerization pathways and isomers, obscuring the actual proportions of C_7 and C_8, as well as C_{10}, C_{11}, and C_{12}. Compared to analogous experiments with 1-butylene, selectivity to gasoline ($S_{Gasoline}$) and kerosene ($S_{Kerosene}$) were defined differently: The gasoline range was extended from $C_{5–9}$ to $C_{5–12}$, since the C_{12} isomers are highly branched and exhibit high octane ratings as well as boiling temperatures according to the gasoline standard. Regarding kerosene, $C_{8–16}$ hydrocarbons were considered, instead of $C_{9–16}$. These fractions were obtained by distillation employing a spinning band column. The gasoline fraction comprised the components up to a boiler temperature of 210°C while the kerosene fraction comprised the components obtained above 150°C. Since there is a considerable overlap of the fractions, several distillation runs were carried out to obtain sufficient quantities for characterization.

The degree of branching was also determined by GC analysis. The product was hydrogenated and the isoindex I_{iso} of the C_8 fraction was determined. It indicates the average number of branchings in octane molecules and is calculated from the mass-related shares x of the branched octanes according to the following formula.

$$\mathrm{I_{iso}C_8} = x_{\mathrm{triple-branched}} \cdot 3 + x_{\mathrm{double-branched}} \cdot 2 + x_{\mathrm{single-branched}}$$

Linear octanes are not considered. For gasoline applications, an isoindex close to 3 is desirable, since this points to triple-branched molecules like isooctane with research octane numbers of around 100.

In the case of co-oligomerization, a long-term experiment lasting for 196 h was carried out. This produced sufficient quantities for the analysis of fuel properties, which was performed for a kerosene and a gasoline fraction at ASG Analytik-Service AG according to certified testing methods. It should be noted that by distillation of the total product mixture, it is not possible to make a clear distinction regarding chain lengths of the products, as the boiling ranges are blurred due to isomers and other effects like boiling delay. Besides distillation no further refining was carried out, which means that the olefinic product mixture was characterized.

3 | Results and Discussion

3.1 | Homo-Oligomerization of Iso-Butylene

Initially, the oligomerization of pure iso-butylene was studied. The influence of different parameters such as catalysts and nickel loading, space velocity, pressure and temperature was investigated to create a reference system that enables comparisons with more complex reaction systems like co-oligomerization reactions of olefin mixtures, which were subsequently investigated. As already mentioned above, dimerization, trimerization, and tetramerization of iso-butylene are primarily expected leading to product mixtures that essentially contain the C_8, C_{12}, and C_{16} oligomers. Experiments with extended reaction times were also carried out to investigate catalyst stability and to obtain sufficient fuel quantities for characterization.

3.1.1 | Influence of Catalysts

The performance of oligomerization catalysts depends on several factors with Brønsted acid sites playing a crucial role in tuning the product distribution. Regarding the nickel-free catalysts, conversions are always above 98% and selectivities to gasoline ($S_{Gasoline}$, $C_{5–12}$) are in a narrow range between 68% and 74% while selectivities to kerosene ($S_{Kerosene}$, $C_{8–16}$) are between 87% and 90% (Table 2). As can be seen for 20/0Ni, fewer acid sites favor the formation of shorter oligomers and the catalyst leads to the highest selectivity to C_{12} and the lowest selectivity to C_{13+}, which mainly consists of C_{16} (Figure 1). At the same time, 20/0Ni yields a lower share of C_9 oligomers in comparison to 40/0Ni and 70/0Ni, which is probably due to a reduction of side reactions taking place on a much smaller scale. In contrast, a higher number of Brønsted acid sites like in 40/0Ni and 70/0Ni leads to an increased formation of higher oligomers, which are dominated by C_{16} compounds. Consequently, this shows that adjusting the

TABLE 2 | Influence of catalysts on iso-butylene conversion and selectivity to gasoline and kerosene.[a]

Catalyst	$X_{\text{iso-Butylene}}$ (%)	S_{Gasoline} ($C_{5\text{–}12}$) (%)	S_{Kerosene} ($C_{8\text{–}16}$) (%)
20/0Ni	99.8	73.7	89.7
20/2Ni	98.7	83.4	85.0
40/0Ni	98.7	70.9	87.2
40/2Ni	98.6	73.5	86.2
70/0Ni	98.9	68.8	88.1
70/2Ni	98.5	79.7	83.8

[a] Reaction conditions: T = 120°C, $p_{\text{Olefin}} = 8$ bar, $p_{\text{total}} = 10$ bar, WHSV = 8 h^{-1}, ToS = 4 h.

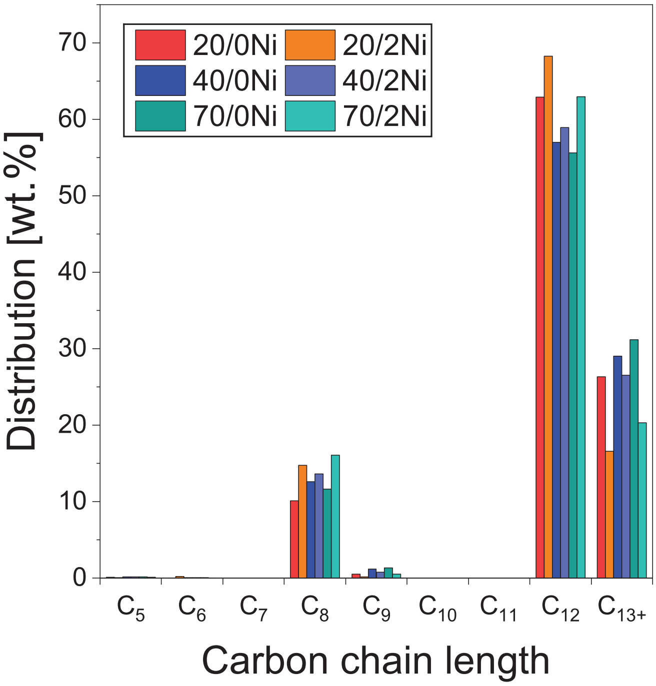

FIGURE 1 | Influence of catalysts on product distribution (T = 120°C, $p_{\text{Olefin}} = 8$ bar, $p_{\text{total}} = 10$ bar, WHSV = 8 h^{-1}, ToS = 4 h).

density of Brønsted sites allows for the tuning of the product distribution and the synthesis of specific oligomers.

In the case of nickel loading, it can be seen that a loading of 2 wt% already changes the product distribution significantly. In principle, the addition of nickel has two effects: It strongly promotes the conversion of ethylene by oligomerization in its coordination sphere and furthermore, it leads to a significant reduction of surface area coming along with the occupancy of Brønsted sites. Consequently, the density of acid sites is reduced, which can be seen from Table 1, and reactions that take place at acid sites are thereby affected. This in turn slightly shifts the product spectra toward shorter chain lengths, which is more pronounced for the catalysts with a lower density of Brønsted acid sites, 20/2Ni and 70/2Ni, than for 40/2Ni with a higher acid site density. Accordingly, nickel loading increases the C_8 and C_{12} fractions while the C_{13+} fraction decreases (Figure 1). This results in an increase in S_{Gasoline} and a decrease in S_{Kerosene} (Table 2). In all cases, molecular branching is high and the isoindex I_{iso} of the C_8 fraction is in a narrow range between 2.95 and 3.00.

3.1.2 | Influence of Process Parameters

To investigate the influence of process parameters catalyst 20/0Ni was chosen, since this catalyst leads to high selectivities towards gasoline and kerosene. Initially, the influence of reaction temperature and iso-butylene partial pressure was investigated. By reducing the temperature from 120°C to 80°C the product spectrum shifts toward C_{12} oligomers whereas the proportions of C_8 and C_{13+} decrease (Figure 2a). Due to the lower C_{16} content, gasoline selectivity (S_{Gasoline}) increases while iso-butylene conversion ($X_{\text{iso-butylene}}$) remains close to 100% (Table 3). In the next step, the partial pressure of iso-butylene was lowered. This was done by increasing the argon content from 20% (Figure 2a) to 60% (Figure 2b), which corresponds to halving the pressure from 8 to 4 bar. In an additional experiment at a partial pressure of 4 bar, the reaction temperature was lowered to 40°C (Figure 2b). A comparison of the results obtained at 80°C with varying iso-butylene partial pressures shows only minor effects on the product spectrum, despite the dilution of iso-butylene. The further lowering of the temperature to 40°C also has only a minor effect on it. However, a trend can be identified whereby the proportion of C_8 decreases with decreasing temperature. Compared to 80°C, the proportion of C_{13+} oligomers is slightly enhanced at 40°C. This can be explained by higher oligomers, which do not desorb as easily from the catalyst surface at lower temperatures. Thus, they remain longer at the acid sites, allowing further oligomerization reactions to higher oligomers.

In addition to temperature and olefin partial pressure, the influence of space velocity (WHSV) was studied employing 20/0Ni as catalyst. Two WHSVs at two pressure levels were investigated. As can be seen from (Figure 3a), the proportions of C_8 and C_{12} increase by doubling the WHSV from 8 h^{-1} to 16 h^{-1} while the proportion of C_{16} oligomers decreases. Consequently, a higher WHSV or shorter residence time leads to shorter oligomers due to shorter contact time of the olefin on the catalyst. This comes along with a higher selectivity to gasoline while selectivity to kerosene decreases (Table 4). A higher pressure shifts the product spectrum slightly from the dimer C_8 to the trimer C_{12} while the proportion of C_{16} remains almost unaffected (Figure 3b). Neither the WHSV nor the pressure have a significant influence on the conversion of iso-butylene. The olefin is almost quantitatively converted in all experiments due to its high reactivity (Table 4).

A comparison of the reaction rates in terms of molar olefin conversion per Brønsted acid sites of the catalyst and second also

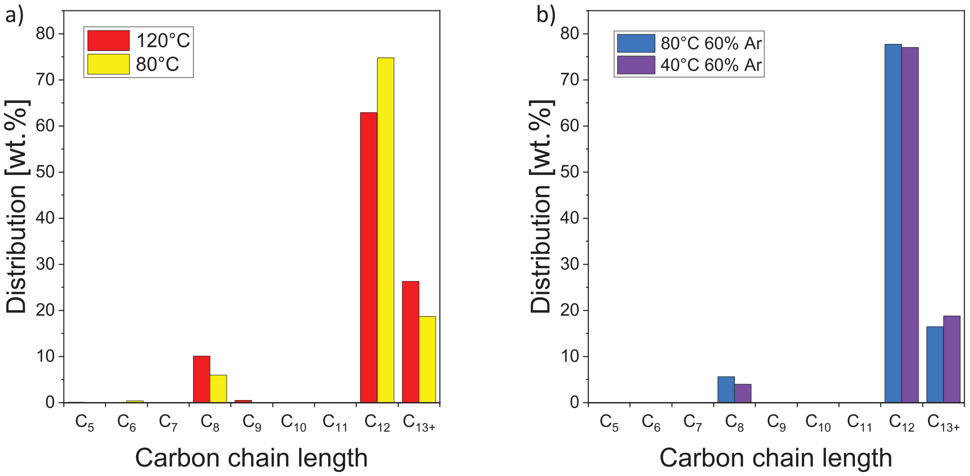

FIGURE 2 | Influence of a) temperature and b) inert gas content on product distribution (Catalyst: 20/0Ni, a) x_{Argon} = 20%, p_{Olefin} = 8 bar, p_{total} = 10 bar, WHSV = 8 h^{-1}, ToS = 4 h; b) x_{Argon} = 60%, p_{Olefin} = 4 bar, p_{total} = 10 bar, WHSV = 8 h^{-1}, ToS = 4 h).

TABLE 3 | Influence of temperature and inert gas content on iso-butylene conversion and selectivity to gasoline and kerosene.[a]

Temperature (°C)	x_{Argon} (%)	$X_{iso\text{-}Butylene}$ (%)	$S_{Gasoline}$ (C_{5-12}) (%)	$S_{Kerosene}$ (C_{8-16}) (%)
120	20	99.8	73.7	89.7
80	20	99.9	81.3	93.5
80	60	99.6	83.5	94.3
40	60	100	81.2	96.0

[a] Reaction conditions: Catalyst 20/0Ni, p_{total} = 10 bar, WHSV = 8 h^{-1}, ToS = 4 h.

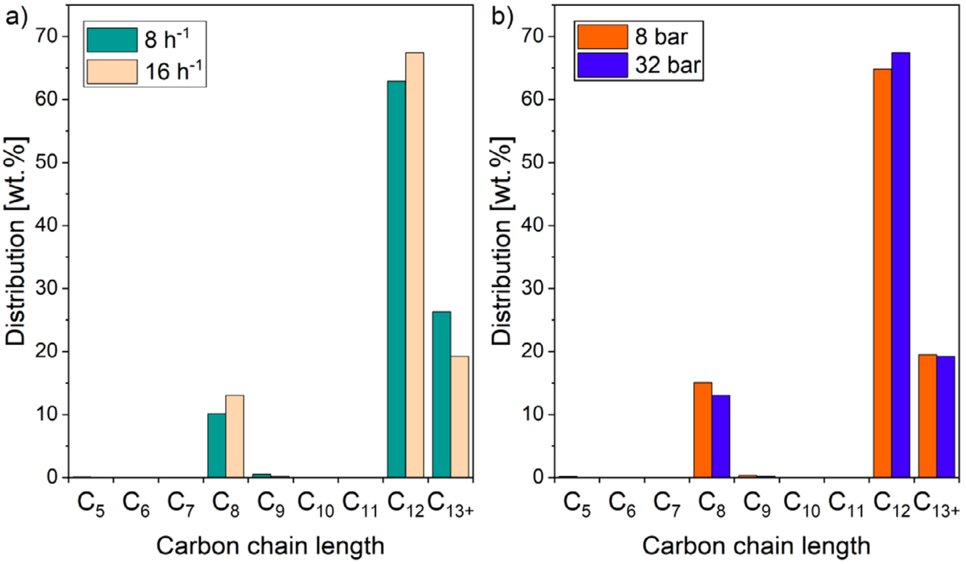

FIGURE 3 | Influence of a) WHSV and b) pressure on product distribution (Catalyst: 20/0Ni, a) T = 120°C, p_{Olefin} = 32 bar, p_{total} = 40 bar, ToS = 4 h; b) T = 120°C, p_{total} = 40 bar, WHSV = 16 h^{-1}, ToS = 4 h).

TABLE 4 | Influence of WHSV and pressure on iso-butylene conversion and selectivity to gasoline and kerosene.[a]

WHSV (h^{-1})	p_{Olefin} (bar)	$X_{iso\text{-}Butylene}$ (%)	$S_{Gasoline}$ (C_{5-12}) (%)	$S_{Kerosene}$ (C_{8-16}) (%)
8	32	99.8	73.7	89.8
16	32	99.8	80.7	86.9
16	8	99.8	80.5	84.7

[a] Reaction conditions: Catalyst 20/0Ni, T = 120°C, p_{total} = 40 bar, ToS = 4 h.

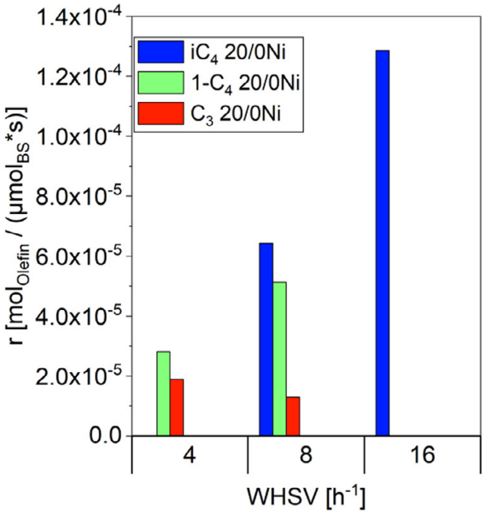

FIGURE 4 | Rate of molar iso-butylene, 1-butylene, and propylene conversion per Brønsted acid sites (BS) of the catalyst and second (Catalyst: 20/0Ni, T = 120°C, $p_{\text{iso-Butylene}}$ = 8 bar, $p_{\text{1-Butylene}}$ = 32 bar, $p_{\text{Propylene}}$ = 32 bar, ToS = 4 h).

shows the superior reactivity of iso-butylene (Figure 4). It should be noted that the corresponding experiments were carried out at an olefin partial pressure of 8 bar in the case of iso-butylene oligomerization while the partial pressure was 32 bar in the case of 1-butylene and propylene oligomerization. Nevertheless, kinetic limitations can be seen for propylene and 1-butylene while the reaction rate increases proportionally to WHSV in the case of iso-butylene, even up to a WHSV of 16 h^{-1}.

To investigate catalyst stability and to produce sufficient fuel quantities for a detailed characterization, ToS was extended to 42 h while a temperature of 120°C, an olefin partial pressure of 8 bar and a WHSV of 16 h^{-1} were set. As for the experiments described above, 20/0Ni was chosen as catalyst since it exhibits the lowest density of Brønsted acid sites of all the nickel-free silica-alumina catalysts studied and consequently leads to the highest selectivity to C_8 and C_{12}. Another aspect is the low deactivation of the catalyst that can be expected due to the reduced formation of long-chain oligomers, which could block the active sites and pores of the catalyst.

No deactivation of the oligomerization catalyst was observed during the experiment and conversion of iso-butylene remained consistently above 98%, indicating a sustained high catalytic activity (Table 5). During 42 h, 4.4 L of product were produced, with 3.25 kg of liquid fuels from 3.3 kg of iso-butylene. The product distribution remained almost unchanged as can be seen from Figure 5 and also the isoindex, which measures the average degree of branching in the C_8 fraction, remained constant at 2.96. With regard to carbon chain length, selectivity to gasoline stayed constant at approximately 80% while selectivity to kerosene stayed around 85%.

3.1.3 | Fuel Properties

Prior to analysis, the product mixture was separated employing a spinning band column. The products up to a maximum boiler temperature of 210°C were assigned to the gasoline fraction. It contains essentially C_8 and C_{12} oligomers while higher oligomers were separated almost quantitatively (Figure 5). The kerosene fraction comprises all products obtained at boiler temperatures above 150°C. It should be noted that the raw product mixture did not boil below 150°C. Even after 1 h at 150°C, evaporation of the C_8 fraction did not occur. This can be explained by a boiling delay of the C_8 fraction since the boiling points of the octenes are around 100°C. As a result, no separation of the C_8 fraction was possible, so it remained in the kerosene fraction. Consequently, the kerosene fraction exhibits the same composition as the crude product, which can therefore be assigned completely to the kerosene fraction.

Some basic properties of the kerosene fraction have been determined and compared to the requirements of the relevant ASTM standard (Table 6). Density as well as smoke point are somewhat too low whereas most of the other properties comply with the standard. The cold properties are particularly noteworthy. The freezing point is below –90°C, which is due to the high degree of branching.

The gasoline fraction was also analyzed and the resulting data were compared to the relevant gasoline standard (Table 7). The RON of 102.4 is remarkably high and can be attributed to the high degree of branching in the oligomers iso-octene and iso-dodecene. The vapor pressure of 7.9 kPa is too low but the other analyzed properties meet the standard. Regarding the boiling characteristics, the transition from the 50% point to the 90% point occurs in a narrow temperature range of 9.3°C, which is due to the high content and evaporation of iso-dodecene.

3.2 | Co-Oligomerization of Iso-Butylene with Ethylene and Propylene

In the next step, co-oligomerization of iso-butylene with ethylene and propylene was investigated. To ensure good comparabil-

TABLE 5 | Influence of ToS on iso-butylene conversion and selectivity to gasoline and kerosene.[a]

ToS (h)	$X_{\text{iso-Butylene}}$ (%)	S_{Gasoline} (C_{5-12}) (%)	S_{Kerosene} (C_{8-16}) (%)
6	99.8	78.5	85.0
24	98.5	79.6	84.8
32	98.8	79.6	85.0
42	98.9	80.3	84.8
Total	99.0	79.5	84.9

[a] Reaction conditions: Catalyst 20/0Ni, T = 120°C, p_{Olefin} = 8 bar, p_{total} = 10 bar, WHSV = 16 h^{-1}.

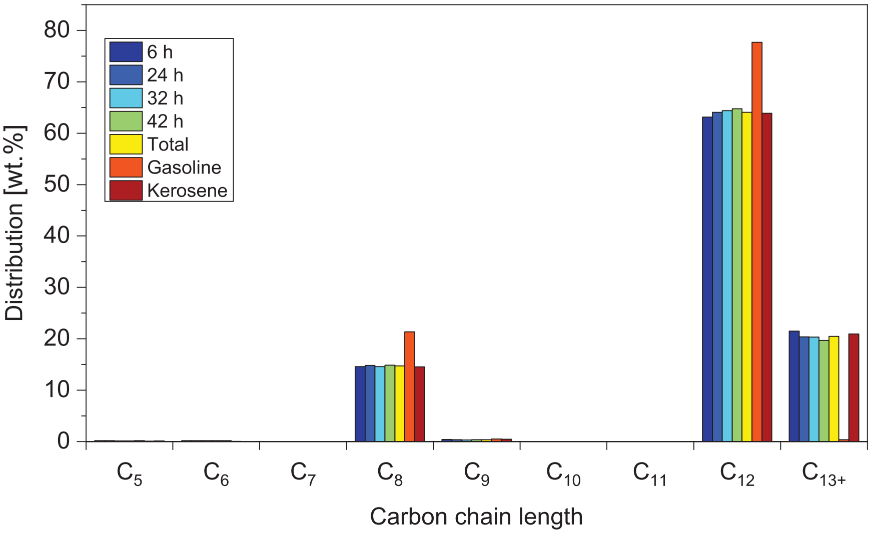

FIGURE 5 | Product distribution as a function of ToS (Catalyst: 20/0Ni, T = 120°C, $p_{Olefin} = 8$ bar, $p_{total} = 10$ bar, WHSV = 16 h^{-1}).

TABLE 6 | Properties of the oligomeric kerosene fraction.

Property	Unit	Oligomeric kerosene	Requirement of ASTM D7566
Acid number	mg KOH/g	0.077	Max. 0.1
Density at 15°C	kg/m^3	768	775 – 840
Flash point	°C	< 40	Min. 38
Freezing point	°C	< −90	Max. −47 (Jet A-1) Max. −40 (Jet A)
Viscosity at −20°C	mm^2/s	4.585	Max. 8
Net heat of combustion	MJ/kg	43.5	Min. 42.8
Smoke point	mm	23.8	Min. 25
Distillation:			
Boiling start	°C	125.6	–
Final boiling point	°C	252.0	< 300
10%-Point	°C	154.6	< 205
50%-Point	°C	177.6	–
90%-Point	°C	215.2	–

ity with previous experiments, similar olefin mixtures were employed containing 40 vol% ethylene, 40 vol% propylene, and 20 vol% iso-butylene, which means that 1-butylene was simply substituted by iso-butylene and the proportions remained the same [41, 44]. For the activation and conversion of ethylene at comparatively low temperature the presence of transition metals, especially nickel, is favorable and therefore, nickel-loaded catalysts were also employed, in addition to the metal-free catalysts, which were predominantly employed in homo-oligomerization. As in the case of homo-oligomerization, important reaction parameters such as temperature, pressure, WHSV and ToS were varied and their influence on conversion, selectivity, and fuel quality was investigated.

3.2.1 | Co-Oligomerization of Ethylene, Propylene, and Iso-Butylene with Metal-Free Catalysts

By employing the nickel-free catalyst 20/0Ni and common reaction conditions, as described for homo-oligomerization, no conversion of ethylene occurs, which is already described in a previous study [44]. Propylene is partially converted while the conversion of iso-butylene is close to 100% (Table 8, Experiment 1). Compared to the homo-oligomerization of iso-butylene, the isoindex I_{iso} C_8 decreases, which is expected due to the higher proportion of di-branched octenes and additional reactions like the conversion of propylene and metathesis reactions.

TABLE 7 | Properties of the oligomeric gasoline fraction.

Property	Unit	Oligomeric gasoline	Requirement of DIN EN228
Research octane number (RON)	–	102.4	95
Density at 15°C	kg/m^3	757.2	720 – 775
Vapor pressure DVPE	kPa	7.9	45 – 90
Distillation:			
Boiling start	°C	109.5	–
Final boiling point	°C	192.1	< 210
10%-Point	°C	137.5	–
50%-Point	°C	172.6	–
90%-Point	°C	181.9	–
Distillation residue	vol%	1.1	< 2

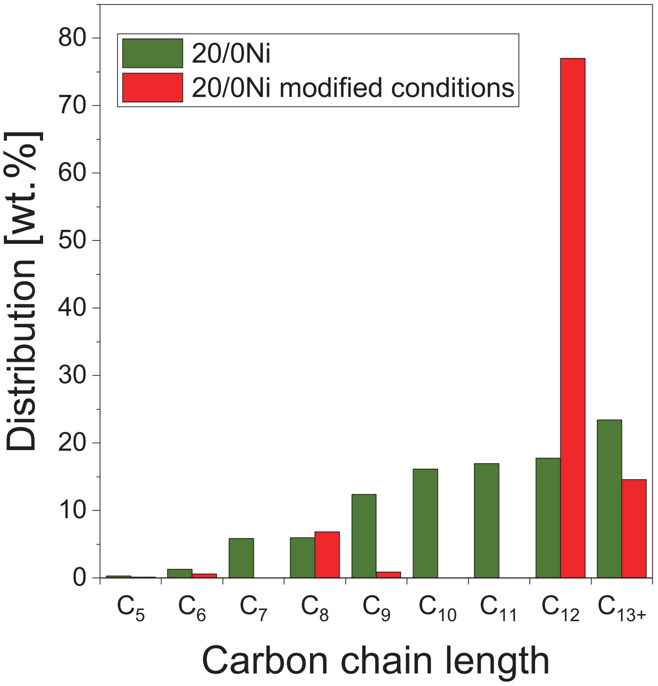

FIGURE 6 | Product distribution for the co-oligomerization of ethylene, propylene, and iso-butylene catalyzed by 20/0Ni under different reaction conditions (Experiment 1 in green: T = 120°C, $x_{\text{Argon}} = 20\%$, WHSV = 4 h^{-1}, $p_{\text{Olefin}} = 32$ bar, $p_{\text{total}} = 40$ bar, ToS = 4 h) and under modified reaction conditions (Experiment 2 in red: T = 80°C, $x_{\text{Argon}} = 60\%$, WHSV = 8 h^{-1}, $p_{\text{Olefin}} = 5$ bar, $p_{\text{total}} = 12.5$ bar, ToS = 4 h).

By varying the reaction conditions, namely lowering the temperature as well as pressure and increasing the WHSV and argon dilution, propylene conversion can be reduced to less than 1% and almost only iso-butylene is being converted (Table 8, Experiment 2). This enables a selective oligomerization of iso-butylene in the presence of ethylene and propylene, which yields the C_{12} trimer as the main component and lower quantities of the C_8 dimer and the C_{16} tetramer (Figure 6). Consequently, iso-butylene can be efficiently separated from such gaseous olefin mixtures by heterogeneously catalyzed oligomerization under mild reaction conditions. The isoindex I_{iso} C_8 is 2.97, which is the same as in the case of homo-oligomerization and which indicates a high molecular branching.

3.2.2 | Influence of Nickel Loading on the Co-Oligomerization of Ethylene, Propylene, and Iso-Butylene

To convert all light olefins, including ethylene, the nickel-loaded catalysts 20/2Ni, 40/2Ni and 70/2Ni were employed under comparatively mild reaction conditions, as described previously for the co-oligomerization of ethylene, propylene, and 1-butylene [44]. In all cases, iso-butylene is completely converted and substantial quantities of ethylene and propylene are also converted (Table 9). Compared to the analogous reactions with 1-butylene in the feed, iso-butylene can promote the conversion of the co-reactants ethylene and propylene. This is the case for catalyst 20/2Ni, the one with the lowest density of Brønsted sites (co-oligomerization of ethylene, propylene, and 1-butylene: $X_{\text{Ethylene}} = 35.0\%$ and $X_{\text{Propylene}} = 21.7\%$). In contrast, for the 40/2Ni and 70/2Ni catalysts, the conversion of ethylene and propylene remains in the same range or decreases compared to the experiments with 1-butylene (40/2Ni: $X_{\text{Ethylene}} = 95.2\%$ and $X_{\text{Propylene}} = 87.7\%$; 70/2Ni: $X_{\text{Ethylene}} = 73.5\%$ and $X_{\text{Propylene}} = 76.2\%$). A possible explanation for this is the significantly higher conversion of iso-butylene and increased reactions at the acid sites. Thus, fewer active sites are available for the conversion of propylene. The decrease in ethylene conversion at nickel sites may also be explained by this. According to Forget et al., ethylene requires a Brønsted site near nickel for oligomerization, so that a synergism between these sites promotes ethylene oligomerization [54]. If the neighboring Brønsted site is already occupied by iso-butylene, ethylene cannot react, which consequently reduces

TABLE 8 | Conversion and selectivity to gasoline and kerosene for the co-oligomerization of ethylene, propylene, and iso-butylene catalyzed by 20/0Ni under common (Experiment 1) and modified (Experiment 2) reaction conditions.

Experiment		Conversion			Selectivity	
No.	X_{Ethylene} (%)	$X_{\text{Propylene}}$ (%)	$X_{\text{iso-Butylene}}$ (%)	S_{Gasoline} (C_{5-12}) (%)	S_{Kerosene} (C_{8-16}) (%)	I_{iso} C_8
1[a]	0	46.5	97.5	41.9	86.6	2.49
2[b]	0	1.0	100	40.1	92.5	2.97

[a] Reaction conditions: T = 120°C, $x_{\text{Argon}} = 20\%$, WHSV = 4 h^{-1}, $p_{\text{Olefin}} = 32$ bar, $p_{\text{total}} = 40$ bar, ToS = 4 h.

[b] Reaction conditions: T = 80°C, $x_{\text{Argon}} = 60\%$, WHSV = 8 h^{-1}, $p_{\text{Olefin}} = 5$ bar, $p_{\text{total}} = 12.5$ bar, ToS = 4 h.

TABLE 9 | Conversion and selectivity to gasoline and kerosene for the co-oligomerization of ethylene, propylene, and iso-butylene with different nickel-loaded catalysts.[a]

Catalyst	**Conversion**			**Selectivity**		
	X_{Ethylene} (%)	$X_{\text{Propylene}}$ (%)	$X_{\text{iso-Butylene}}$ (%)	S_{Gasoline} ($C_{5–12}$) (%)	S_{Kerosene} ($C_{8–16}$) (%)	I_{iso} C_8
20/2Ni	54.5	38.6	100	52.3	74.5	2.48
40/2Ni	87.4	88.8	100	41.6	82.3	2.25
70/2Ni	28.2	74.3	100	39.7	85.2	2.36

[a] Reaction conditions: T = 120°C, $x_{\text{Argon}} = 20\%$, WHSV = 4 h^{-1}, $p_{\text{Olefin}} = 32$ bar, $p_{\text{total}} = 40$ bar, ToS = 4 h.

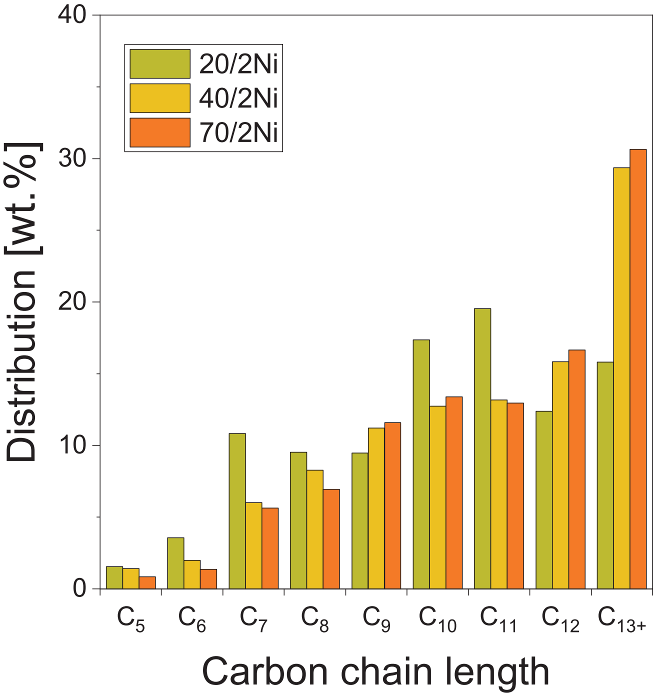

FIGURE 7 | Product distribution for the co-oligomerization of ethylene, propylene, and iso-butylene with different nickel-loaded catalysts (T = 120°C, $x_{\text{Argon}} = 20\%$, WHSV = 4 h^{-1}, $p_{\text{Olefin}} = 32$ bar, $p_{\text{total}} = 40$ bar, ToS = 4 h).

ethylene conversion. Another reason may be the blockage of pores, which restricts access to active centers. As can be seen from Figure 7, long-chain oligomers in the C_{13+} region are formed on 40/2Ni, as in the case of 70/2Ni, with a proportion of about 30% in each case. This represents a relative increase of 66% compared to 1-butylene co-oligomerization and argues for a faster deactivation of the catalyst in terms of active site occupancy. This difference is due to the increased conversion of the butylene component in the case of iso-butylene. The catalyst 20/2Ni is an exception since the product distributions change only slightly here. In particular, the absolute deviation of the proportion of C_{13+} is less than 1%. Nevertheless, a slight shift of the product distribution toward longer oligomers due to the increased iso-butylene conversion can be observed here as well. In summary, it can be stated that not only the catalysts and process parameters have a significant influence on catalytic performance, but also the feed compositions and the resulting products, as shown by the direct comparison of ethylene/propylene/iso-butylene co-oligomerization with ethylene/propylene/1-butylene co-oligomerization.

3.2.3 | Long-Term Experiment

A long-term experiment lasting for 196 h was conducted to investigate how the co-oligomerization of ethylene, propylene, and iso-butylene compares to the corresponding co-oligomerization with 1-butylene. Regarding the catalyst, 40/2Ni was chosen and, to enable maximum comparability, the same reaction conditions were employed.

Conversions of the individual olefins over ToS were recorded and iso-butylene conversion remains constant at nearly 100% reflecting again the much higher reactivity of iso-butylene compared to the other olefins (Figure 8). The decrease in the conversions of ethylene and propylene is most likely due to the high conversion of iso-butylene, which leads to increased filling of the catalyst pores by its oligomers. This in turn can result in the formation of a liquid film and a limitation of mass transfer. Therefore, the accessibility of ethylene and propylene to the active centers could be impeded, resulting in lower conversions compared to the co-oligomerization with 1-butylene [44]. Additionally, the decrease in conversions, especially at higher ToS, could be explained by deposition of higher oligomers on the catalyst, which block the pores and active sites. Regarding ethylene, conversion is in the range from approximately 72% to 90%. It is notable that in the co-oligomerization with 1-butylene, ethylene conversion is well over 90% throughout the entire ToS, without or with minor diffusive limitations [44]. Regarding propylene, the decline in conversion is more pronounced with iso-butylene, so that after 100 h, approximately 50% of the propylene has reacted, while with 1-butylene, approximately 75% of the propylene has reacted.

The catalyst was regenerated after 100 h ToS at ambient pressure and 300°C under an argon flow of 200 mL/min. This allowed the original activity of the catalyst to be completely restored and this applies to both, conversions (Figure 8) as well as product distributions (Figure 9). Complete regeneration of the catalyst could not be achieved in the case of 1-butylene and this behavior could be explained by the higher liquid formation in the case of iso-butylene, which can be seen as ambivalent: On the one hand, liquid formation impairs catalytic activity by limiting mass transport, and on the other hand, it facilitates catalyst regeneration by reducing the formation of long-chain oligomers and simplifying the desorption of such components from the catalyst surface. With regard to product distributions, it should be noted again that the actual chain length distribution is obscured by deviating boiling points of highly branched molecules. Thus, it is also to be expected that proportions of C_7 are trimethylpentenes, as well as proportions of C_{10} and C_{11} belong to the C_{12} fraction. However,

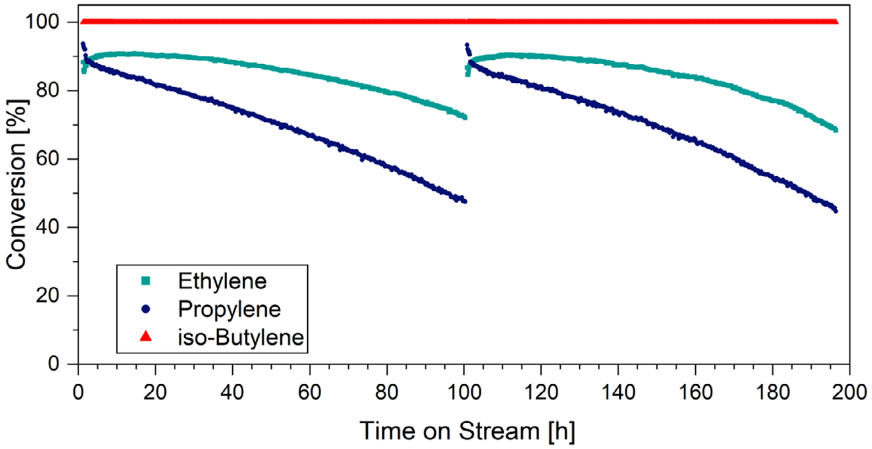

FIGURE 8 | Olefin conversion over ToS with catalyst 40/2Ni (T = 120°C, $x_{\text{Argon}} = 20\%$, WHSV = 4 h^{-1}, $p_{\text{Olefin}} = 32$ bar, $p_{\text{total}} = 40$ bar).

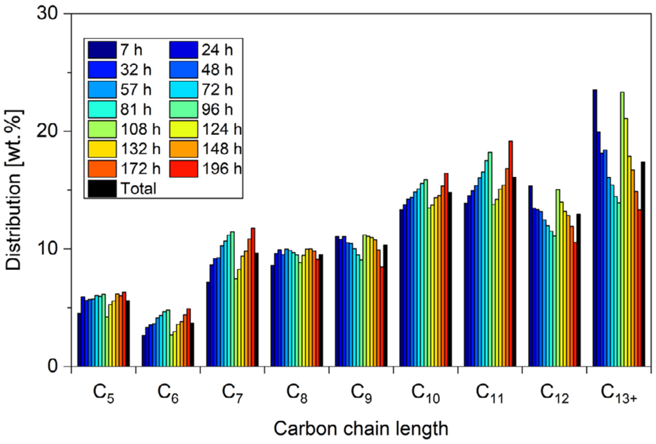

FIGURE 9 | Development of the product distribution over ToS with catalyst 40/2Ni (T = 120°C, $x_{\text{Argon}} = 20\%$, WHSV = 4 h^{-1}, $p_{\text{Olefin}} = 32$ bar, $p_{\text{total}} = 40$ bar).

some main characteristics and trends become obvious (Figures 8 and 9): 1. The product spectrum after catalyst regeneration is essentially the same as in the beginning of the experiment. 2. Regarding the overall product mixture (Figure 9, black columns), the C_{13+} fraction accounts for the largest share, closely followed by the C_{11}, C_{10}, C_{12}, and C_9 fractions. 3. Regarding changes over ToS, the formation of lower oligomers ($C_{5\text{–}11}$) increases overall with increasing ToS while the formation of higher oligomers (C_{12} and C_{13+}) decreases. This behavior was also observed in the co-oligomerization of 1-butylene with the difference that the formation of lower olefins increases up to C_9 while the formation of higher olefins decreases from C_{10} on, which was justified by the blocking of acid sites [44].

3.2.4 | Fuel Properties

As part of the long-term experiment described in the previous chapter the isoindex was also determined as a function of ToS (Figure 10). It is a useful measure of the molecular branching in the C_8 fraction and thus an indicator of the octane rating of the resulting gasoline. In contrast to the co-oligomerization with 1-butylene, the isoindex rises during the experiment until regeneration and also after regeneration. This is probably due to the reduced conversion of ethylene and propylene, resulting in reduced proportions of low-branched oligomers. This comes along with an increase in the influence of iso-butylene oligomerization and an increase in the average degree of branching of the products. After regeneration, ethylene and propylene conversion returns to the initial values (Figure 8), which is reflected by a decrease in the isoindex followed by an increase as in the initial phase of the experiment. The isoindex of the total product is 2.29, which is significantly higher than in the case of 1-butylene co-oligomerization, where an isoindex of 1.79 was determined [44]. As already mentioned above, a higher branching is usually beneficial, especially in terms of combustion behavior and cold properties. The resulting physico-chemical as well as fuel properties are discussed in the following.

For the analysis of the fuel fractions, gasoline, and kerosene were separated by distillation, analogous to the homo-oligomerization of iso-butylene. As in the case of homo-oligomerization, the fraction up to a boiler temperature of 210°C was assigned to gasoline and the fraction obtained above 150°C was assigned to kerosene. Regarding the molecular composition, the gasoline fraction contains all components up to C_{12} while the kerosene fraction essentially contains all components from C_7 on (Figure 11). This results in a selectivity to gasoline (S_{Gasoline}) of 82.6% and a selectivity to kerosene (S_{Kerosene}) of 90.7%. It should be noted that no further refinement of the products was carried out and the raw products were used for subsequent characterization.

Several properties of the oligomeric kerosene are listed in Table 10 and compared to the requirements of the relevant standard. The properties are largely within the specifications of the standard, with only the density and smoke point being slightly too low. However, these parameters could possibly be adjusted by blending. It is remarkable that, compared to co-oligomerization with 1-butylene, the freezing point could be significantly lowered from −38°C to below −90°C. This once again demonstrates the positive influence of iso-butylene as a C_4 feed.

The properties of the associated gasoline comply largely with the standard, with the exception of the vapor pressure being

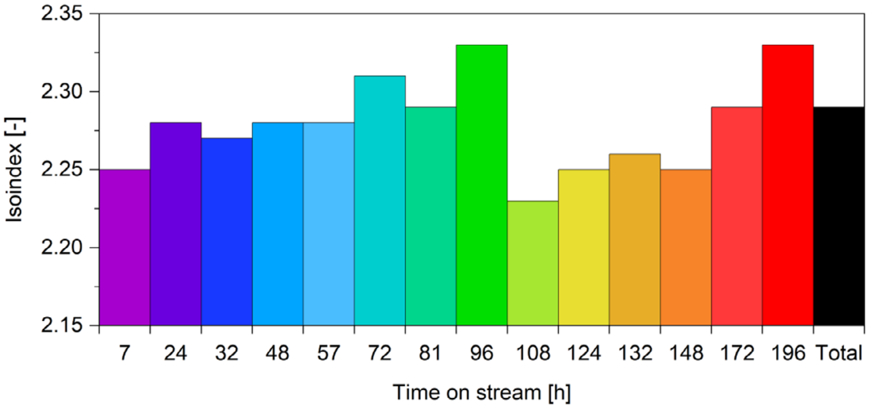

FIGURE 10 | Development of the isoindex of the C_8 fraction over ToS (T = 120°C, $x_{Argon} = 20\%$, WHSV = 4 h^{-1}, p_{Olefin} = 32 bar, p_{total} = 40 bar).

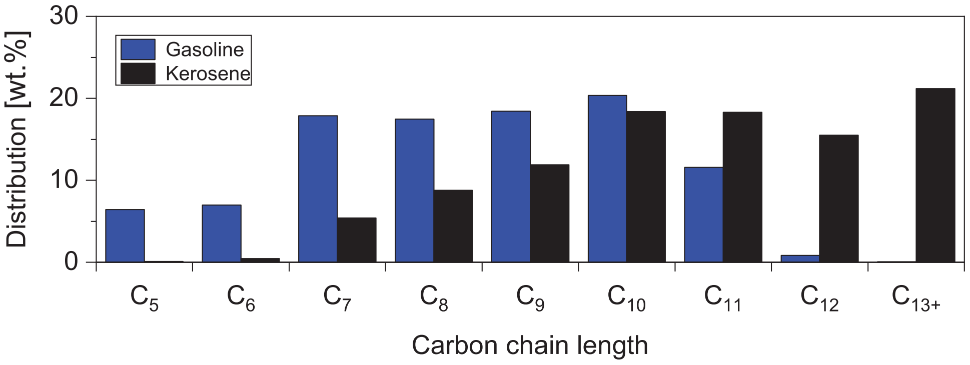

FIGURE 11 | Product distributions of the gasoline and kerosene fractions.

TABLE 10 | Properties of the oligomeric kerosene fraction.

Property	Unit	Oligomeric kerosene	Requirement of ASTM D7566
Acid number	mg KOH/g	0.029	Max. 0.1
Density at 15°C	kg/m^3	772.9	775 – 840
Flash point	°C	< 40	Min. 38
Freezing point	°C	< –90	Max. –47 (Jet A-1) Max. –40 (Jet A)
Viscosity at –20°C	mm^2/s	3.711	Max. 8
Net heat of combustion	MJ/kg	43.5	Min. 42.8
Smoke point	mm	23.5	Min. 25
Distillation:			
Boiling start	°C	117.3	–
Final boiling point	°C	298.4	< 300
10%-Point	°C	139.0	< 205
50%-Point	°C	179.8	–
90%-Point	°C	244.8	–

TABLE 11 | Properties of the oligomeric gasoline fraction.

Property	Unit	Oligomeric gasoline	Requirement of DIN EN228
Research octane number (RON)	–	97.2	95
Density at 15°C	kg/m^3	736.7	720 – 775
Vapor pressure DVPE	kPa	26.1	45 – 90
Distillation:			
Boiling start	°C	48.0	–
Final boiling point	°C	180.1	< 210
10%-Point	°C	90.1	–
50%-Point	°C	135.4	–
90%-Point	°C	167.7	–
Distillation residue	vol%	1.1	< 2

too low (Table 11). However, complete standard compliance could possibly be achieved through blending, as in the case of oligomeric kerosene. Compared to the co-oligomerization with 1-butylene, the octane rating in terms of RON increases from 95.2 to 97.2. It should be considered, that the standard allows for 18 vol% of olefins, so this oligomeric gasoline can only be used after blending or hydrogenation. After hydrogenation, higher blending shares are possible but the RON decreases, since paraffins usually lead to lower RON compared to the corresponding olefins.

4 | Conclusions

Iso-butylene is a suitable building block for the synthesis of hydrocarbon fuels like gasoline and kerosene. The heterogeneously catalyzed homo-oligomerization of iso-butylene has been investigated employing silica-alumina-based catalysts. Thereby, iso-butylene can be selectively converted under mild reaction conditions to its integer multiples C_8, C_{12}, and C_{16}. Due to its molecular structure, iso-butylene shows very high reactivity, so almost quantitative conversion was observed in all experiments. The selectivity to kerosene components is very high since the main fraction is composed of C_{12} olefins, which are produced in proportions of up to 80%. Selectivities to kerosene reached 96% while selectivities to gasoline reached 83%. By varying the reaction conditions, the contents of the individual oligomers can be varied and thus, the product spectrum can be shifted slightly between gasoline and kerosene. Oligomerization experiments over a ToS of 42 h showed constant conversion of iso-butylene with constant product distribution. Analyses of the gasoline and kerosene fractions showed promising properties, especially a high RON of 102 in the case of gasoline and a freezing point below −90°C in the case of kerosene. These favorable properties can be attributed to the high molecular branching and make the fractions valuable fuels, at least for blending purposes.

Besides homo-oligomerization, co-oligomerization of iso-butylene with ethylene and propylene is also a promising opportunity to produce fuels with high molecular branching. Employing nickel-loaded silica-alumina catalysts, all olefin species can be converted under mild reaction conditions. Selectivities to kerosene up to 92% and selectivities to gasoline up to 83% were reached. The average degree of branching in the C_8 fractions is significantly higher compared to oligomers obtained by the co-oligomerization of 1-butylene with ethylene and propylene. As in the case of homo-oligomerization, the use of iso-butylene contributes to better fuel qualities, for example, in terms of octane number or cold flow properties, which are crucial for kerosene applications. As a result, a RON of 97 and a freezing point below −90°C were reached. Due to the much higher reactivity of iso-butylene compared to propylene and ethylene, it is possible to separate iso-butylene from such olefin mixtures by oligomerizing it to liquid fuels under mild reaction conditions while ethylene and propylene do not react. A long-term test over 196 h showed continuous deactivation of the catalyst concerning the conversion of ethylene and propylene, whereas iso-butylene is almost quantitatively and steadily converted. Due to the decreasing conversion of ethylene and propylene, the conversion of iso-butylene dominates, which increases the isoindex over time. However, the catalyst can be fully reactivated by heating. The analyses of the produced gasoline and kerosene showed promising properties, especially considering that no further refining was carried out. The results are significant in the context of producing fuels without aromatics. There, the losses in fuel quality caused by the lack of aromatics need to be compensated by the other fuel components.

Ongoing work concentrates on the catalysts and includes enhancing catalyst stability, for example, by catalyst shaping, reactivating spent catalysts and also developing new catalyst systems beyond the mixed oxides presented here. With regard to the olefins, varying feed compositions and the recycling of nonconverted olefins or unwanted oligomers are considered, to enable a high tolerance concerning the feed compositions while maintaining a high selectivity concerning the desired products. Another focus is on maximizing fuel yield and quality according to the relevant standards while minimizing the need for additional refining steps. The results will support concepts for the scaling up of fuel production and contribute to a reliable assessment of the entire process chain from the raw materials to the usable fuels. Provided that the olefins stem from renewable resources, the pathways investigated should be very well suited for the production of Sustainable Aviation Fuels (SAF).

Acknowledgments

The authors gratefully acknowledge financial support from the Federal Ministry of Transport / Fachagentur Nachwachsende Rohstoffe (FNR), Germany, within the joint research project “Renewable Fuels from Green Refineries of the Future” (REF4FU, FKZ: 16RK24001B). Furthermore, the authors thank Sasol for providing catalyst materials and Marius Drexler for technical support.

Open access funding enabled and organized by Projekt DEAL.

Author Contributions

Constantin Fuchs: Data curation; formal analysis; investigation; methodology; writing – original draft. **Ulrich Arnold**: Conceptualization (equal); funding acquisition (equal); project administration (equal); supervision (equal); writing – review & editing (equal). **Jörg Sauer**: Conceptualization (equal); funding acquisition (equal); project administration (equal); supervision (equal); writing – review & editing (equal).

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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