icarus

INTERNATIONAL COOPERATION FOR
SUSTAINABLE AVIATION BIOFUELS

D1.3 Overview of the VC Isobutanol to SAF

Task 1.3: Isobutanol to SAF value chains –

WP1: Framework conditions for SAF development in Europe and MICs
March 2024

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EXECUTIVE SUMMARY

Icarus – International cooperation for sustainable aviation biofuels - is a Horizon Europe project that aims at accelerating the scale-up of sustainable aviation biofuels production, in order to support the EU goals for climate mitigation in 2030 and 2050 and the ReFuelEU Aviation, enhance the potential to export European renewable fuel technologies into global developing markets, and improve sustainability of aviation fuels while reducing their cost worldwide.

The core activity of **Icarus** is to address the whole value chains of three Sustainable Aviation Fuel (SAF) production routes by improving, with innovative solutions, critical and limiting technology steps, and by performing techno-economic, environmental, and social assessments for the complete valuechains. Bringing together European expertise on the entire value chains for SAF production and including Mission Innovation countries (MIC): Canada, India, Brazil, and USA (as member of the EEAB) the project will develop best practices (based on improved innovative technologies) and concepts (founded on market access knowledge) along entire value chains.

This 1.3. deliverable deals on two major aspects for SAF production from isobutanol: i) fermentative processes to produce isobutanol from biomass-derived carbohydrates; ii) the thermocatalytic production of isobutanol into molecules relevant for SAF production. This deliverable deals on description of state-of-the-art and challenges, aiming to have a detailed overview that will later allow the definition of the research tasks defined in ICARUS related to isobutanol production or SAF production via similar routes.

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1 Isobutanol production

2.1. Introduction

Isobutanol is a four Carbon aliphatic alcohol, that can be produced chemically or biologically. Biological production of isobutanol by fermentation is a preferred route due to the environmental impact of chemical methods. However, fermentative isobutanol production has several challenges, including low titer, low productivity, and high toxicity of the isobutanol to the fermenting microorganism. A number of studies have been undertaken to tackle these challenges, by engineering different microorganisms for high isobutanol production.

2.2. Microorganisms used for isobutanol production

No organism has been identified that naturally produces isobutanol at a level suitable for industrial application. However, several microorganisms are known to naturally produce traces of isobutanol. These organisms have been used as a starting organism to engineer higher isobutanol production through modification of the isobutanol pathway. The most common microorganisms explored include the bacteria *Escherichia coli*, *Bacillus subtilis*, and *Corynebacterium glutamicum*, and the yeast *Saccharomyces cerevisiae*.

So far, the most promising results have been obtained by engineered *E. coli*. Liao's group have succeeded in developing an *E. coli* strain with a significantly improved isobutanol production level. They modified the amino acid biosynthesis pathway and diverted the intermediate 2-ketoacid into isobutanol through several genetic modifications. The final strains produced up to 22g/L isobutanol with a yield of 0.35g/g glucose (Atsumi, Hanai, and Liao 2008).

In the yeast *S. cerevisiae*, isobutanol is naturally produced in trace amounts, via the enzymes of valine biosynthesis and Ehrlich pathway. In addition, *S. cerevisiae* is inherently more robust and is tolerant to various alcohols than bacteria. Although a much higher isobutanol level has been achieved in engineered bacteria, metabolic engineering of *S. cerevisiae* for higher isobutanol production continues to be of great interest. This is because, yeast is much more tolerant than bacteria to various alcohols, and therefore, a much higher isobutanol titer could be produced if the isobutanol pathway is properly optimized.

2.3. Engineering S. cerevisiae for isobutanol production

One of the limiting factors in metabolic engineering of isobutanol production pathway in yeast is the subcellular compartmentalization of the pathway. Unlike bacteria, the isobutanol pathway in yeast is partitioned both in the cytosol and mitochondria. First, the cytosolic pyruvate has to be imported into the mitochondria. Through few enzymatic cascades, pyruvate is converted in to 2-ketoisovalerate (2-KIV), which is then exported back to the cytosol and channeled into isobutanol in two steps of enzymatic reactions. To overcome this challenge, several studies have been undertaken by relocating the whole pathway, either to the mitochondria or to the cytosol.

Compartmentalization of the isobutanol pathway to the mitochondria improved the isobutanol production in S. cerevisiae (Avalos, Fink, and Stephanopoulos 2013; Yuan and Ching 2015). However, the applicability of this system is limited due to poor well differentiated mitochondria in cells exposed to industrial fermentation condition, including poor aeration, and high sugar level. For that reason, engineered cytosolic isobutanol pathway seems more promising. Indeed, studies have shown a higher isobutanol titer by over-expressing cytosolic enzymes, in the absence or in the presence of the mitochondrial pathway (Brat et al. 2012). However, a much higher isobutanol titer of up to 0.6g/L has been obtained when the mitochondrial pathway and the valine biosynthesis pathway is blocked.

Another challenge of engineering yeast for isobutanol production is the competitive pathway of ethanol production. Ethanol is a major fermentation product in *S. cerevisiae*. Although ethanol production can easily be abolished by deleting the three structural pyruvate decarboxylase (PDC) genes, pdc-negative strains suffer from inability to grow in high glucose levels and require a C2 carbon source, like ethanol or acetate. In some cases, glucose is even toxic to pdc-negative strains. To overcome that, evolutionary engineering of the PDC-minus isobutanol strains with gradual increase in the glucose level resulted in improved strains with the ability to grow in high glucose levels. This has been mainly related to mutations in the MTH1 gene, a transcription regulator involved in glucose sensing (Oud et al. 2012). More recently, a stategy where isobutanol is produced together with ethanol in strain without PDC deletion has been proposed. That way, isobutanol can be produced at a higher rate compared to strains with PDC deletion (Lima et al. 2023). However, the isobutanol yield per consumed sugar is lower because the sugars go to ethanol production. Additionally, a separation process for isobutanol and ethanol is required, probably increasing the cost of downstream processing.

2.4. Improving isobutanol production by in situ product removal.

A high isobutanol titer is one of the most important parameter for economic feasibility of isobutanol production process. A major limiting factor against achieving high isobutanol titer is the cytotoxicity of isobutanol. It has been shown that isobutanol hinders growth of *E.coli* when the concentration exceeds 8g/L, though it continues to produce isobutanol above that concentration (Brynildsen and Liao 2009). The isobutanol tolerance of the *E. coli* has been improved through screening and evolutionary adaptation. However, improved isobutanol tolerance did not correlated to improved isobutanol production.

On the other hand, *S. cerevisiae* has better tolerate to isobutanol than bacteria, which is around 2% isobutanol. Nevertheless, most microorganism generally have a tolerance limit of 2% (Knoshaug and Zhang 2009). For that reason, in situ removal of isobutanol during fermentation is the best alternative for obtaining a high isobutanol titer. Baez and colleagues, implemented in situ isobutanol removal from a bioreactor, using gas stripping method and achieved an isobutanol titer of 50g/L in 72h (Baez, Cho, and Liao 2011).

A more recent development to improve isobutanol production titer is the establishment of a cell free system, where all the reaction taking only with purified enzymes without cells. For that purpose, several steps of optimization and selection of the optimal enzymes have been performed and an isobutanol titer of 275g/L has been achieved with a yield of 95% in 5 days (Sherkhanov et al. 2020). This groundbreaking work has achieved a very high isobutanol titer with a yield and productivity that exceeds the current 1st generation ethanol production. However, the cost of the process is currently extremely high, due to the cost and stability of enzymes and cofactors required for the process. Until another groundbreaking discovery for cost reduction of the cell free system is achieved, cell based fermentation with in situ recovery seems to be the most feasible way to produce isobutanol.

2.5. Isobutanol production from lignocellulose

Lignocellulose biomass, such as agricultural wastes and forest residues are attractive sources of feed stocks for environmentally sustainable biofuel production, including isobutanol. Such feed stocks contain a high proportion of the C5 sugar xylose, the second most abundant sugar, next to glucose. However, native strains of *S. cerevisiae* are unable to utilize xylose. There have been several metabolic engineering studies undertaken to develop yeast strains with xylose utilization capacity. Lane et al. 2020, engineered the isobutanol pathway using a xylose utilizing strains that was previously developed for ethanol production. They achieved a 2.6g/L isobutanol in an optimized bioreactor and flask fermentation condition. Interestingly, the isobutanol production from xylose in this strain was much better compared to isobutanol production from glucose. It has been shown that xylose utilization is not completely directed towards ethanol, as is the case for glucose, probably because xylose doesn't elicit the Crabtree effect. For that reason, a higher yield of isobutanol is achieved from xylose than from glucose.

Songdech and colleagues, also attained an isobutanol titer of about 0.1g/L from xylose, using a strain that was engineered for high xylose utilization and improved isobutanol pathway (Songdech et al. 2024). In that report, using a bioreactor optimization and with addition of Iron, 15g/L of isobutanol has been produced with a yield of 0.15g/g xylose. The high isobutanol production due to the addition of Iron in the medium is probably due to the dependence of the enzyme dihydroxyacid dehydratases (Ilv3) on Fe/S cluster (US8017376). This also indicated that optimal fermentation conditions are important to reach a high isobutanol titer.

2.6. Industrial production of isobutanol

Gevo, Butamax and Green Biologics pioneered the isobutanol production from biomass. (Roussos et al. 2019). After Green Biologics announced its closure (https://biomassmagazine.com/articles/green-biologics-to-cease-operations-16319), and Gevo acquired Butamax's isobutanol related patents (https://biomassmagazine.com/articles/gevo-acquires-patents-from-butamax-receives-new-us-patent-18353), Gevo remains the only or dominant player in isobutanol production technologies.

Gevo implements an integrated system of isobutanol production with the existing corn ethanol plant. In the corn ethanol plant, the corn mash stream supplies both the ethanol and the isobutanol fermentation tanks. Once the corn mash goes into the isobutanol fermentation tank, Gevo's proprietary yeast is added to start the fermentation. While the yeast converts the C6 sugar into isobutanol, isobutanol is continuously removed to keep the isobutanol below the toxicity level for the yeast. This way, a high isobutanol titer is achieved, that is more suitable for further purification (https://gevo.com/wp-content/uploads/2023/03/Gevo-Whitepaper-Overview-of-Gevos-Biobased-Isobutanol-Production-Process.pdf).

To our knowledge, there is no industry producing isobutanol from lignocellulosic sugar yet. Possible limitations include the complex nature of lignocellulose material and the release of inhibitory compounds during pre-treatment and hydrolysis the complex lignocellulose material. Unlike 1st generation feed stocks, like corn, which have only C6 sugar that are readily fermented by most microorganisms, lignocellulose materials also contain C5 sugars, primarily xylose, that are not fermented by *S. cerevisiae*. For that reason, robust microorganisms are needed that are able to ferment both C5 and C6 sugar, cope with the high inhibitors in the lignocellulose hydrolysate, and able to produce isobutanol at high rate and yield.

Gevo's 1st generation yeast can produce very good amount of isobutanol from 1st generation feed stock. NovelYeast has developed superior 2G ethanol strain with very good inhibitor tolerance and xylose utilization capacity. Combining the two strains with genome shuffling and evolutionary adaptation, NovelYeast has developed a robust isobutanol strain that can produce isobutanol from C5 and C6 sugar from lignocellulose biomass. This paved a way for the realization of the 2G isobutanol production.

One limitation, however, is the high cost of enzymes to hydrolyze lignocellulosic material, which range between 20 and 25% of the overall production cost in ethanol production process. To overcome this, NovelYeast, the ICARUS project, will develop cellulase secretion capacity in the 2G isobutanol strain that it developed. Although it is difficult to completely eliminate the use of commercial enzymes, development of cellulolytic enzyme secreting 2G isobutanol strain should be able to significantly reduce the amounts of commercial enzymes used. This will contribute to the feasibility of the realizing commercial 2G isobutanol production.

2 Isobutanol to jet

2.1. Commercial scale production

The separation of alcohol products from the stream obtained from fermentation yields both economic inputs but also operational costs. The primary water/alcohol separation is performed via distillation, and the product purity is limited by the water/alcohol azeotrope. Isobutanol leads to a heterogeneous azeotrope with two liquid phases. Pure alcohol streams demand decanters coupled to stripping columns. However, SAF production facilities may even stand water contents in the 1-5% range, avoiding the use of energy-intensive and costly distillation stages, especially considering that the dehydration catalysts used in SAF production processes are tolerant to significant amounts of water.

The commercial production of jet from isobutanol is based on three distinct catalytic steps, designed in such way at different conditions and using catalytic materials: alcohol dehydration into the corresponding olefin, the oligomerization of light olefin into SAF range olefins, and their hydrogenation, followed by fractionation of the synthetic paraffin product[1]. Traditionally such olefin oligomerization commonly produces a variety of liquid fuels including gasoline and diesel, and thus further adjustments of the catalytic operation allows generating hydrocarbons in the SAF range as well. In practice, a mixture of synthetic paraffins in the kerosene range is formed, which is fractioned off to produce a viable jet blendstock and the remaining cuts are used naphtha and/or diesel range products. As an example, the commercial process of GEVO company is illustrated in *Figure 1*.

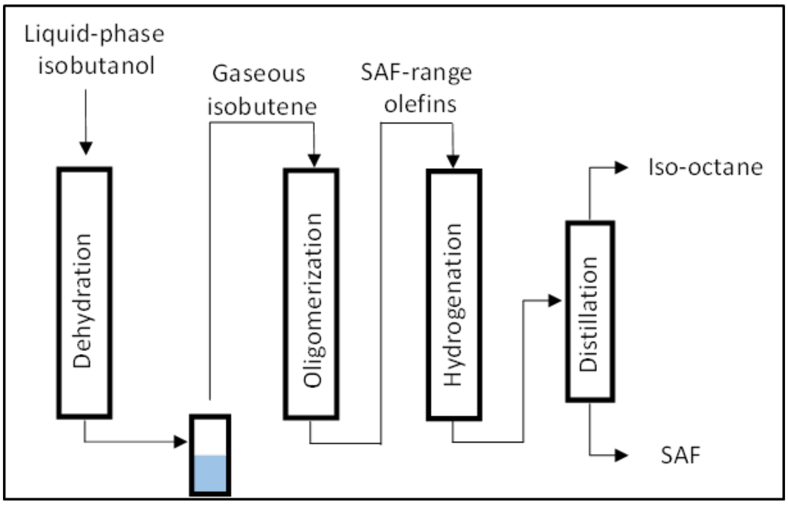


Figure 1. GEVO´s commercial process for SAF production from isobutanol[1.]

Among the alcohol-derived SAFs available in the market, GEVO has attained certified standards for blending up to 30% of this SAF with fossil-derived kerosene. This achievement is an indicator of the market´s potential for such products[2].

2.2. One-pot synthesis

Some research efforts aim to integrate the entire process into a single stage. However, the water produced during dehydration may present challenges for subsequent oligomerization processes.

In 2019, Du and co-workers[3] carried out a study on different reaction conditions using HZSM-5 catalysts for isobutanol conversion, aiming to tune the product selectivity towards olefins and aromatics.

To perform the reaction, HZSM-5 zeolites with different molar ratios of SiO_2/Al_2O_3, as well as a series of HZSM-5 containing Ga were synthetized. The optimum reaction conditions were as follows; a fed of isobutanol of 0.01 ml/min, a temperature of 400 °C, isobutanol partial pressure of 1.63% in N_2 and a WHSV of 1.25 h^{-1}.

The authors observed that when using the original H-ZSM-5, mild conditions favoured the production of olefins, while more severe conditions led to the formation of aromatics. However, olefins of more than C_8 could not be obtained, and the resultant butenes undergo reversible oligomerization and cracking reactions, leading to a mixture of C2-C6 olefins. The following *Figure 2* shows the conversions and selectivities obtained with the different Ga-loaded catalysts.

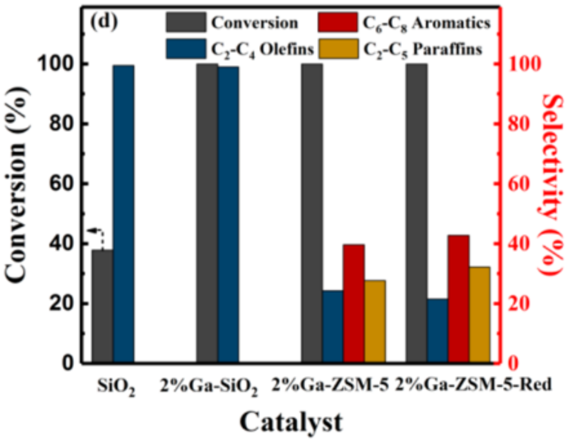


Figure 2. Product distribution comparison among different catalysts.

On the other hand, as for Ga-SiO_2, which contained mainly Lewis acids generated from Ga_2O_3 particles, it was able to selectively convert isobutanol to butenes. However, when Ga was impregnated into HZSM-5, it significantly enhanced the formation of aromatics by enhancing the direct dehydrogenation reaction.

It was observed that the water produced by the dehydration of isobutanol played a negative role in the transformation of Ga species from their active to inactive forms. This could be the reason for the ineffectiveness of Ga in reducing the selectivity of unwanted low-valent kerosenes.

Guo and co-workers[4] investigated the catalytic oligomerization of isobutanol to liquid hydrocarbons using different commercial catalysts such as H-Y, Al-MCM-41, H-MOR and H-SAPO-34 in a batch reactor. The reaction conditions employed were as follows: 10 ml of isobutyl alcohol, reaction temperature of 240 °C, reaction time of 4h, 0.5 g of catalyst and a 1.0 MPa of N_2 feed gas.

The authors concluded that the SAPO-34 zeolite´s deactivation was attributed to the presence of micropores, while the Al-MCM-41 zeolite was also unsuitable for the dehydration process due to its limited presence of weak acid sites. On the other hand, H-MOR zeolite demonstrated optimal performance at 240 °C, as illustrated in *Figure 3*. Over the course of the reaction, isobutanol conversion increased rapidly within the initial 4 hours, rising from 30% to 82%, before gradually reaching a maximum conversion of 94% after 10 hours. Concurrently, the selectivity towards C_{9+} olefin production increased with reaction time, reaching a maximum value of 20%.

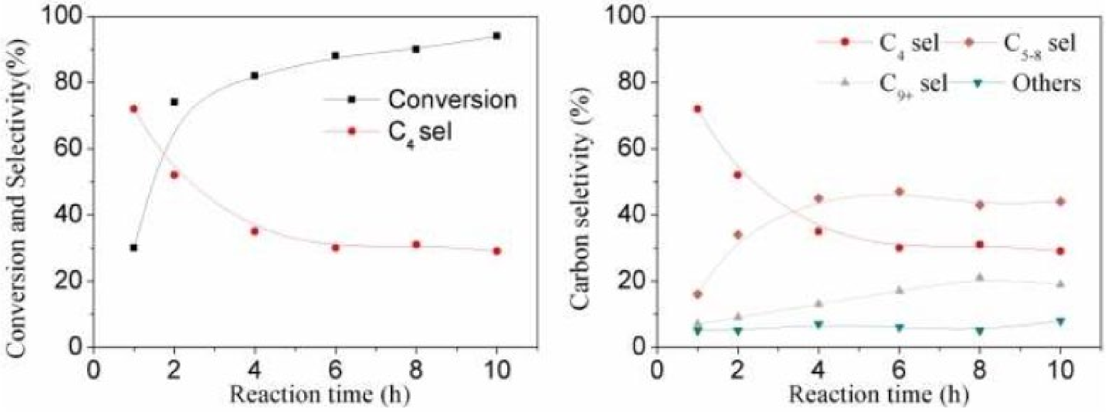


Figure 3. Catalytic performance of isobutyl alcohol oligomerization with varied reaction time (reaction conditions: isobutyl alcohol 10 ml; reaction temperature 240 °C, catalyst weight: 0.5 g; loaded gas N_2 1.0 MPa).

Following the investigation, Guo´s group[5] carried out the oligomerization reaction of isobutyl alcohol over Beta zeolite catalysts treated by various dealumination methods, which provided a possible avenue to develop a promising catalyst.

The reaction was carried out in a batch reactor, with 10 ml of isobutyl alcohol and 0.5 g of catalyst, at a pressure of 1.0 MPa N_2, a temperature of 240 °C and a reaction time of 4 hours. Previously, the catalyst was treated with HCl or EDTA to dealuminate it.

Among the catalysts tested, the HCl_{2h}-BEA catalyst showed the highest conversion, reaching 98%, as well as the highest selectivity towards C8-C16 carbon chain products, yielding 59%. The obtained results are shown in the *Figure 4.*

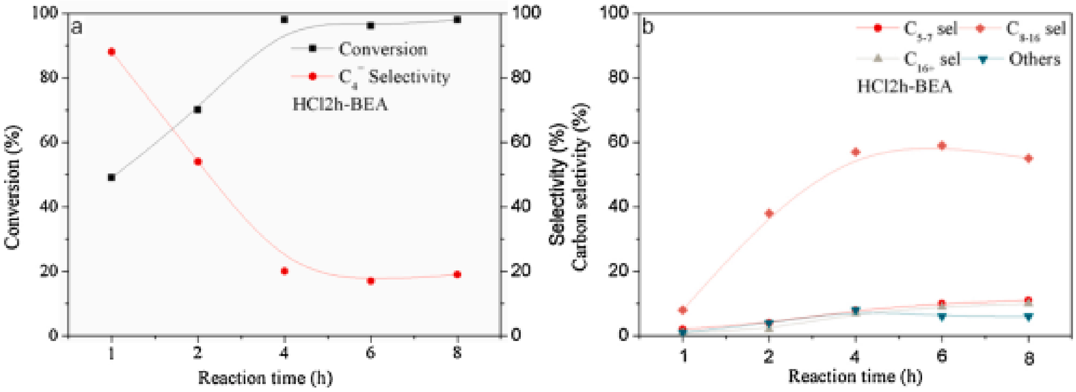


Figure 4. The effect of reaction time on isobutyl alcohol oligomerization over HCl_{2h}-BEA (reaction conditions: 10 ml isobutyl alcohol; 0.5 g_{cat}; 10 MPa N_2; reaction temperature 240 °C)

It was concluded that through the dealumination process, the extra aluminium and impurities were removed. As a result, the pores of the zeolite became smoother, which further improved their catalytic activity. In addition, a reduction in the total amount of acid sites and the number of Brønsted acid sites in the zeolite was observed. Moreover, it was found that a higher proportion of Lewis/ Brønsted acid sited was needed to promote the oligomerization reaction step to form jet fuels. At the same time, this promotion of the oligomerization reaction also facilitated the dehydration reaction of isobutyl alcohol.

In 2023, Zhang et al.[6] demonstrated a selective synthesis of jet fuel from ABE or low carbon alcohols by coupling a two-step process under atmospheric pressure. When the ionic liquid catalyst was used, directional synthesis of jet fuels was achieved by polymerization of olefins at room temperature and atmospheric pressure. The zeolite catalysts used for the dehydration process were SAPO-34, HZSM-5, AlMCM-41 and H-Beta, and the ionic liquid used for the oligomerization process was [Bmim]Cl-2AlCl3.

As mentioned, the process consisted of two stages, first the dehydration of the alcohol, at temperatures of 350 °C. The conversions of isobutanol were almost 100% with all the catalyst, and selectivities to isobutene around 20%. On the other hand, olefin polymerization was carried out using the ionic liquid [Bmim]Cl-2AlCl3 at 25 °C for 2 hours. As for the results obtained, when fed with isobutene, the conversions to C12 and C16 were 35% and 22%, respectively. The authors commented that the main factors affecting jet fuel selectivity and performance included catalyst type, reaction temperature and reaction time.

2.3. Dehydration of isobutanol to isobutene

Dehydration reactions of alcohols using solid catalysts have been studied and documented in the literature since the beginning of the 20th century. The most common dehydration of isobutanol is carried out using slightly acidic γ-alumina catalysts. However, numerous catalysts for isobutanol dehydration have been investigated over the years, including zeolites, acid resins and others[7].

In research conducted by Taylor and co-workers[7], the dehydration of isobutanol was investigated employing both commercial and modified alumina-based catalysts. The investigation encompassed two primary catalyst types: firstly, powder form commercial γ-alumina (referred to as Catalysts A), and secondly, a commercial catalyst with ring structure (denoted as Catalyst B). Subsequently, these commercial catalysts were modified aimed at reducing the silica content to slightly enhance the acidity. The modified powder catalyst was designated as Catalyst C, whereas the modified structured catalyst was labelled as Catalyst D.

In each experiment, wet isobutanol (10% w/w water) was fed into the reaction system at atmospheric pressure, with a reaction space velocity (WHSV) of 5 h^{-1}. The results of isobutanol conversion and selectivity towards isobutene obtained by each catalyst are presented in *Figure 5.*

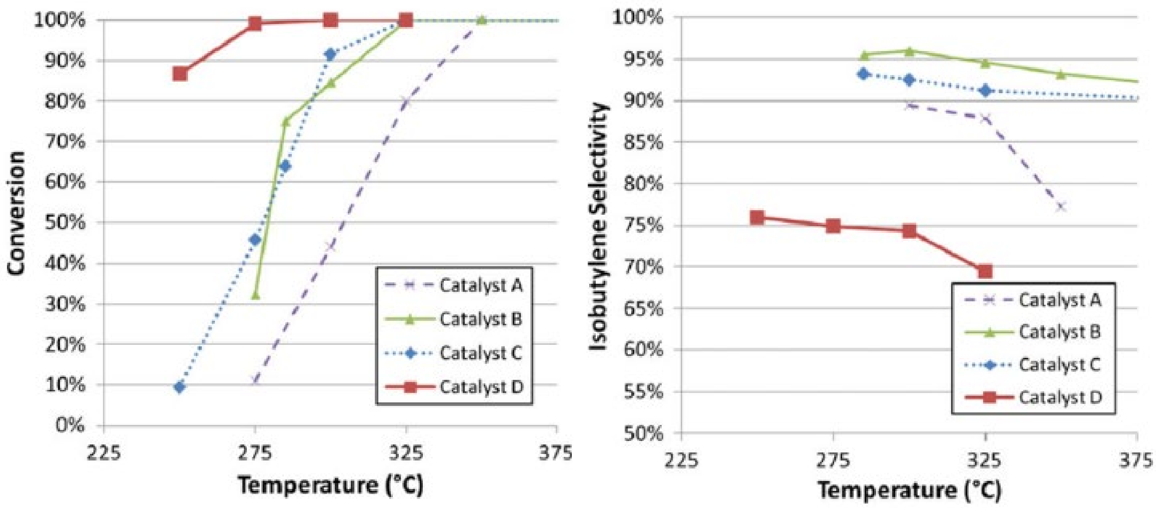


Figure 5. Conversion of isobutanol (left) and selectivity of isobutene (right) over different catalysts (Catalyst A: commercial powder alumina, Catalyst B: commercial ring structured alumina, Catalyst C: modified powder alumina, Catalyst D: modified ring structured alumina).

As can be observed in the results, γ-alumina catalyst A required higher temperatures to achieve good conversion and showed low selectivity towards isobutene. On the other hand, catalyst D showed the best conversion at lower temperatures, although it had the lowest selectivity towards isobutene. This effect could be attributable to the high acidity observed in this catalyst. In contrast, catalysts B and C exhibited the best combination of high conversion and good selectivity towards isobutene. In the case of the catalyst B, it demonstrates the highest selectivity across all temperatures, making it preferred choice for applications requiring maximum isobutylene yield. Conversely, for downstream processes where linear butenes are favoured, D should be the suitable dehydration catalyst.

Furthermore, the study investigated the impact of pressure, water content, and isobutanol fermentation impurities on the catalytic activity. In terms of pressure, it exerted a negative effect on conversion at low temperatures, and it was accompanied by slightly higher selectivity. However, at high temperatures, higher pressure did not significantly affect either conversion or selectivity.

Regarding the effect of water content, at low temperatures, the water content of isobutanol had a negative effect on the conversion and caused a slight increase in the selectivity of isobutene. However, at higher temperatures, almost complete conversion was observed for all water contents and no significant change in selectivity. Finally, concerning the common types of fermentation impurities examined, it was found that they do not negatively impact the dehydration of isobutanol.

In 2017, Gunst et al.[8] investigated the conversion of three butanol isomers: 1-butanol, 2-butanol and isobutanol. They employed H-ZSM-5 as an acid catalyst, which has been extensively studied for various dehydration reactions and is known for its high stability and activity.

To investigate the effect of the temperature on the product distribution in the conversion of isobutanol, the selectivity was studied in a broad range of conversions at temperatures ranging from 493 to 513 K as shown in *Figure 6.* A stable product selectivity was observed for different reaction temperatures, even at minimal (lower than 15%) and high (exceeding 80%) conversion rates.

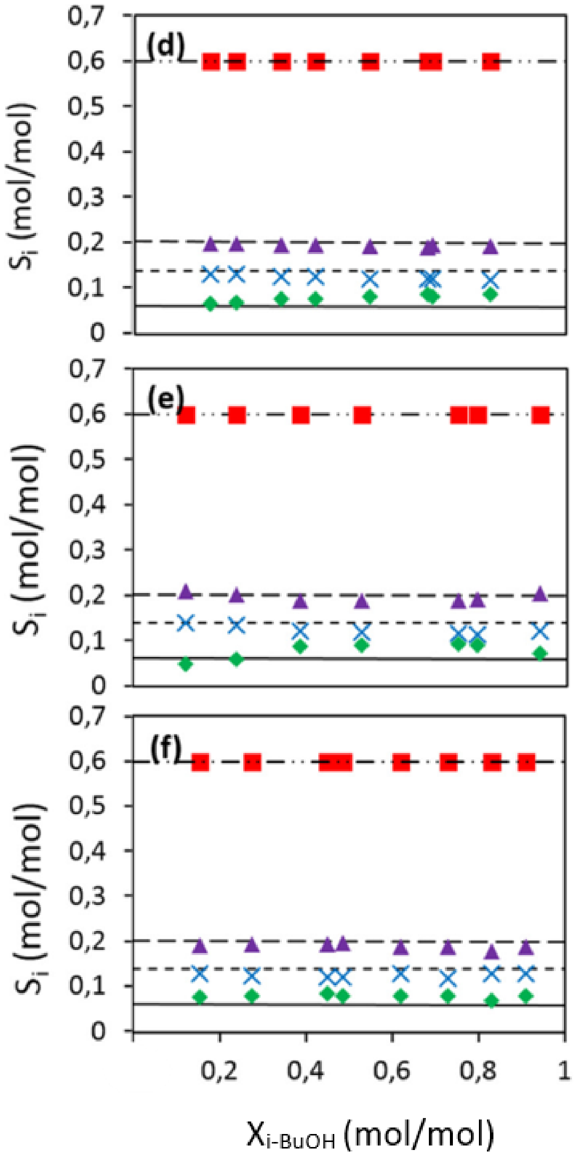


Figure 6. Selectivity (S_i) as function of conversion ($X_{i\text{-}BuOH}$) for isobutanol at (d) 513 K, (e) 503 K and (f) 493 K. 🟥 = iso-butene, ◆ = 1-butene, ✖ = cis-butene, ▲ = trans-butene. Common reaction conditions: $P°_{i\text{-}BuOH}$ = 29 kPa.

The formation of isobutene was accompanied by rapid double bond and skeletal isomerization of butene isomers, even at low conversion. On the other hand, no significant effect of temperature on product selectivity was observed, due to this rapid isomerization and the absence of any di-alkyl-ether intermediates.

The effect of water content was also studied. It was observed, that isobutanol did not show any change in activity of the dehydration reaction when additional water was present. No negative effect on selectivity or conversion was found with this excess water.

Finally, the authors conclude that, regardless of the butanol isomer studied, high selectivities towards butenes were detected under mild reaction conditions. However, it was highlighted that isobutanol was the most promising option. This isomer is the only one that does not shed secondary products or intermediates, directly producing isobutene. For this reason, is the most promising among the four isomers of butene. Additionally, the zeolite H-ZSM-5 exhibited great potential as a catalyst for these reactions, owing to its high activity and minimal deactivation.

Buniazet and co-workers[9] carried out an evaluation of the medium pore ferrierite zeolite (FER) as a catalyst in the dehydration of isobutanol to butenes. It is well known for its activity and high selectivity in skeletal isomerization of n-butene to isobutene. In their study, they investigated the influence of several reaction parameters, including temperature, contact time and time on stream, as well as the addition of water to the reaction.

Figure 7 shows the evolution of isobutanol conversion, selectivity and the proportion of linear butenes, as well as the carbon balance at 250 °C. The results showed that FER was selective towards isobutenes, with an average selectivity value of 25% and remains constant over time. for 24.

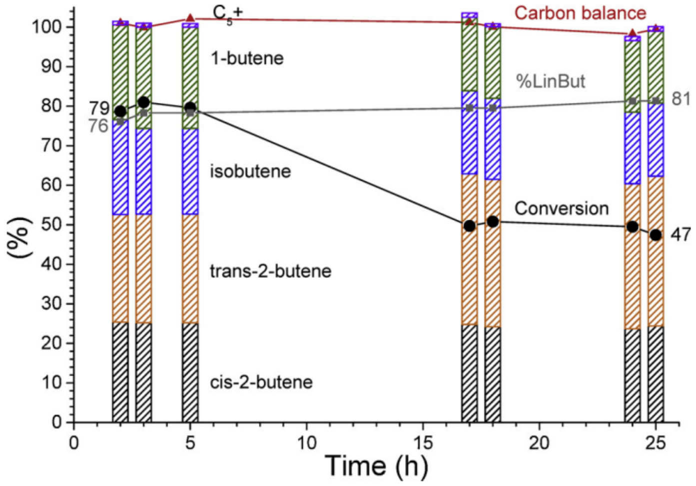


Figure 7. Evolution with time in operation of the conversion, butene selectivity and values of %LinBut and carbon balance of ferrierite at 250 °C, iC_4OH/inert: 30/70 y 1/WHSV 0.07 h

On the other hand, regarding the effect of water on the reaction, it was observed that water added or generated by dehydration had no impact on the textural and structural properties of FER under the reaction conditions over the reaction time. However, water was found to positively influence the catalytic activity at temperatures below 250 °C and negatively at higher temperatures, possibly due to competitive adsorption between water and isobutanol.

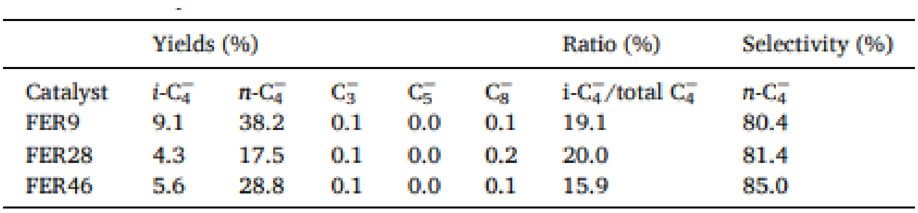
Unexpectedly, when water was introduced into the feed at low contact times, there was a notably higher proportion of linear butenes. This was due to a decreased tendency to form isobutene and an increased preference for 1-butene. Indeed, water's role may involve inhibiting the prototropic shift of isobutylcarbenium ions or saturating the deprotonation sites responsible for isobutene formation. A similar effect was observed for water generated in situ during the dehydration stage, although to a lesser extent (high conversion case). It could be that, alongside water, the development of soft coke also hinders the formation of isobutene.

Similarly, Van Daele and co-workers[10] carried out an exploration of the direct conversion of isobutanol to n-butenes using the previously mentioned FER. This process involved a cascade reaction in which dehydration of isobutanol was followed by skeletal isomerization of the primary products, carried out at low temperature (< 573 K) to mitigate catalyst deactivation.

Firstly, five catalysts including γ-Al_2O_3, and four zeolites of different structures (ERI, FER, TON and MFI) were evaluated in isobutanol conversion. It was observed that both the activity and n-butene selectivity of all zeolites were significantly higher than those of γ-Al_2O_3, which might suggest that the confinement in the zeolite porosity or the strong Brønsted acidity promoted the n-butene selectivity.

Among the zeolites evaluated, FER showed excellent activity and the highest selectivity towards n-butenes (81.4% at 50% conversion). The results obtained by dehydration/isomerization of isobutanol are detailed in *Table 3.*

Table 3. Iosbutanol dehydration/isomerization on FER zeolites.



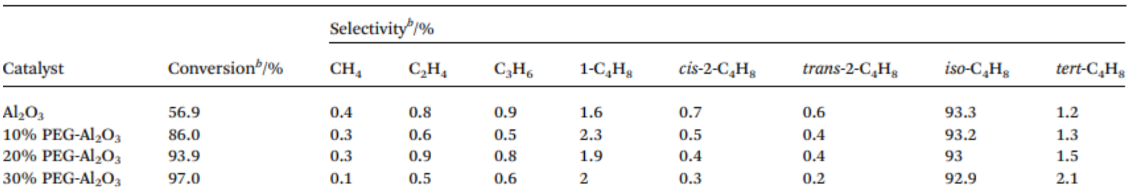
	Yields (%)					Ratio (%)	Selectivity (%)
Catalyst	i-$C_4^=$	n-$C_4^=$	$C_3^=$	$C_5^=$	$C_8^=$	i-$C_4^=$/total $C_4^=$	n-$C_4^=$
FER9	9.1	38.2	0.1	0.0	0.1	19.1	80.4
FER28	4.3	17.5	0.1	0.0	0.2	20.0	81.4
FER46	5.6	28.8	0.1	0.0	0.1	15.9	85.0

[a]at 50% isobutanol conversion in a PFR, reaction conditions T= 523 K, WHSV= 100 h^{-1}, P_{atm}= 1 bar, $P_{isobutanol}$= 45 mbar, TOS= 4 h.

In conclusion, the combination of catalytic tests allowed them to stablish that neither isobutanol nor isobutene penetrated the internal structure of FER. However, a linear relationship was found between the Brønsted acid sited located on the external surface and the dehydration rate constant. Therefore, they suggested that these acid sites were the active dehydration sites of isobutanol.

In 2021, Tian´s group[11] investigated the correlation between polyethylene glycol, employed as a low-cost pore-forming agent, and its impact on the structure of Al_2O_3 and its catalytic performance. The modified alumina was used as a catalyst for the dehydration reaction of isobutanol, aiming to obtain a highly active and selective catalyst for isobutene production. *Table 4* complied the data obtained from the activity tests of the different PEG-modified alumina catalysts.

Table 4. Dehydration of isobutanol over PEG-modified catalysts[a]



		Selectivity[b]/%							
Catalyst	Conversion[b]/%	CH_4	C_2H_4	C_3H_6	1-C_4H_8	*cis*-2-C_4H_8	*trans*-2-C_4H_8	*iso*-C_4H_8	*tert*-C_4H_8
Al_2O_3	56.9	0.4	0.8	0.9	1.6	0.7	0.6	93.3	1.2
10% PEG-Al_2O_3	86.0	0.3	0.6	0.5	2.3	0.5	0.4	93.2	1.3
20% PEG-Al_2O_3	93.9	0.3	0.9	0.8	1.9	0.4	0.4	93	1.5
30% PEG-Al_2O_3	97.0	0.1	0.5	0.6	2	0.3	0.2	92.9	2.1

[a]Reaction conditions: P= 0.1 MPa; T= 330 °C; LHSV= 12 h^{-1}. [b]Average activity in the initial 24 hours.

It was concluded that the pore structure of activated alumina catalyst had a significant effect on the dehydration performance of isobutanol to isobutene. The addition of PEG during the catalyst preparation did not affect the crystalline structure of the catalyst but notably modified the porosity, resulting in the formation of macropores.

Likewise, the isobutanol dehydration performance of the catalyst was better when a 30% pore expander was added to the activated alumina catalyst. The conversion was enhanced up to 97%, while mantaining a constant selectivity of 93%. Under the optimal reaction conditions - temperature at 330 °C, pressure at 0.1 MPa and WHSV of 12 h^{-1} , the catalyst was stable for 24 hours.

Finally, Dubois et al[12], presented a review summarizing the scientific and patent literature on the selective dehydration reaction of isobutanol to isobutene testing different types of alumina as catalysts. The data collected showed that the experimental conditions and the design of the catalytic process had a great impact on the overall performance of the catalytic systems for this reaction.

In addition, it was observed that the choice of low- or high- pressure conditions for the selective dehydration of isobutanol to isobutene affected not only the subsequent recovery and purification of isobutene, but also the stability of the catalyst. Due to the strong inhibition of alumina catalysts by water vapor, the high-pressure reaction required longer contact times and larger catalyst volume. Therefore, the alumina catalysts needed to have good hydrothermal stability to avoid rapid deactivation. The impact of water partial pressure on catalytic dehydration was also described and shown to affect side reactions.

On the other hand, to minimize the loss of catalyst surface area during the reaction, it was suggested that it would be necessary to reduce the water vapor pressure and lower the reaction temperature. However, since water is a reaction product and cannot be completely removed, product separation is facilitated when dehydration is carried out at higher pressures. Under such conditions, a sufficiently high temperature was required to achieve nearly complete conversion.

2.4. Oligomerization of isobutene

The oligomerization of light alkenes is an important and widely studied area in the petroleum industry, as it represents a route to produce a variety of heavier weight compounds used in motor fuels, lubricants, plasticizers, pharmaceuticals, dyes, resins, detergents and additives. This process occurs through a complex network of reactions over acid sites. The distribution of the products is regulated by thermodynamic constraints that favor carbon-carbon bond formation over cleavage at higher pressures and lower temperatures[13].

Commonly employed heterogeneous solid acid catalysts for olefin oligomerization include zeolites, sulfonic acid resins, solid phosphoric acid, heteropolyacids and sulfonated zirconia. In recent years, zeolites and sulfonic resins have received increased attention for the conversion of olefins to combustible hydrocarbons[14].

In 2028, Kocaman´s research group[15], examined the alterations in structural properties of TPA/MCM-41 catalysts across a range of TPA (tungstophosphoric acid) loadings, from 1 to 90 wt%, and their impacts on isobutene oligomerization performance were also investigated.

The reaction was conducted at a temperature of 343 K, with the reactor pressurized to 15 bars. Isobutene was fed into the reactor at a rate of 0.3 ml/min, resulting in an isobutene conversion of over 75%. The selectivities achieved with each TPA loading are presented in *Figure 8.*

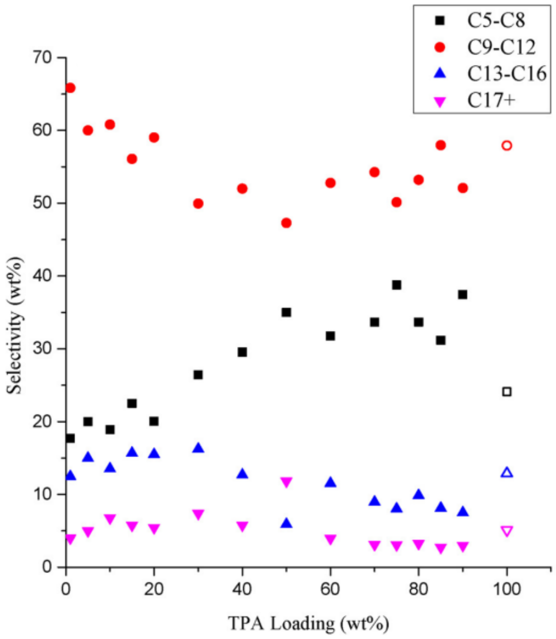


Figure 8. The variation of product selectivities with TPA loadings.

Authors concluded that these results highlight a notable advantage of the MCM-41 support, which provides a high degree of dispersion for these super acids due to their significantly large surface area.

Saavedra et al.[14] evaluated the use of several H-form zeolites (H-beta, H-Y, USY and H-ZSM-5) and sulfonic polymeric resins (Amberlyst-36 and CT275) as catalysts for oligomerization reaction of olefins. Firstly, the authors evaluated the synthesis of olefins by a dehydration of aqueous ethanol feedstock using a Zn1Zr2.5Oz mixed oxide catalyst, followed by the oligomerization of olefins. On the other hand, the oligomerization of propene and isobutene intermediates was also studied. The scheme of the process is shown in *Figure 9*.

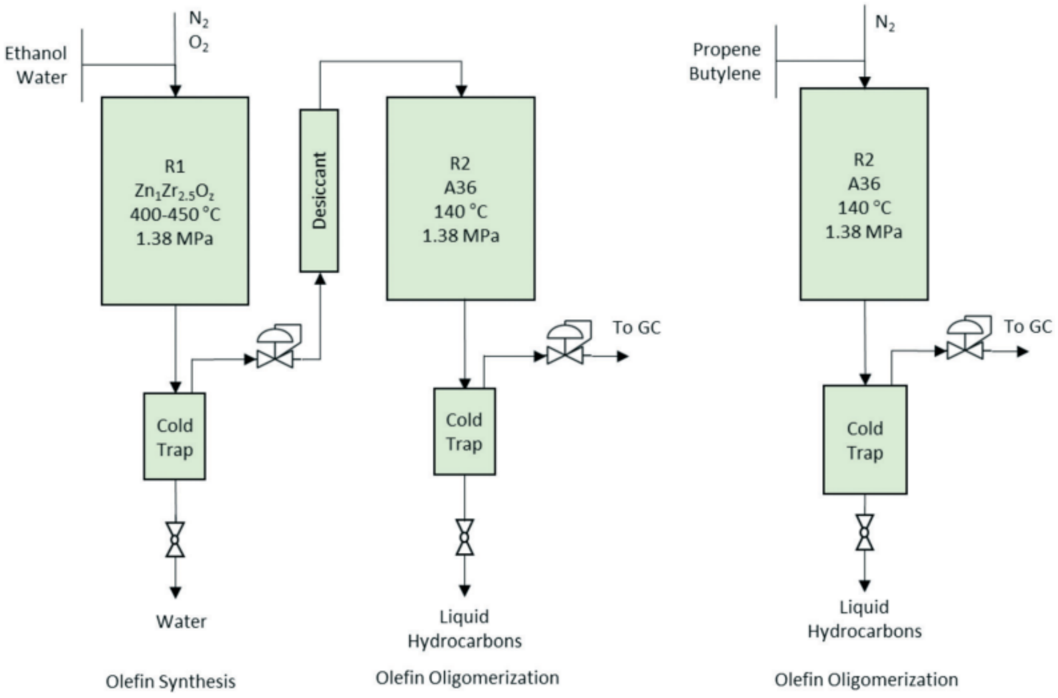


Figure 9. Simplified process flow diagrams illustrating the bench-scale packed bed reactors employed for (A) integrated olefin production (R1) and oligomerization (R2), and (B) model olefin oligomerization (R2).

Among the olefins obtained by the first process, the selectivity to isobutene was about 44%. For the oligomerization of olefins, as mentioned before, different H-form zeolites and resins were studied. It was shown that the H-beta zeolite, which showed a higher acid capacity compared to the other zeolites, Amberlyst-36 and CT275, had conversions to isobutene above 99% in different temperatures.

It was concluded that, both H-beta and CT275, were active, selective and stable (for at least 20 hours) to produce hydrocarbons from the fuel range, in yields of 87% and 84% respectively. In the case of the H-beta zeolite, it produced longer, and less branched carbon chains compared to those obtained with the CT275. This could be attributed to the higher acidity presented by CT275, which mainly facilitated isomerization reactions. In addition, the higher temperature used with H-beta (200 °C) compared to CT275 (120 °C) facilitated other reactions that resulted in a broader carbon number distribution.

In the same year, Al-Kinany and co-workers[16], developed a novel phosphoric acid supported on H zeolite-Y for isobutene oligomerization. The authors, investigate the impact of temperature on isobutene conversion and oligomer distribution across a range of 50-100ºC. This variation was explored due to the highly exothermic nature of the isobutene oligomerization reaction.

Experiments were conducted at temperatures of 50 °C, 75 °C, and 100 °C, with a space velocity of 175.3 h-1, under atmospheric pressure conditions. Under these parameters, the phosphoric acid supported on H-ZSM-Y exhibited the highest isobutene conversion rate at 50 °C as shown in *Figure 10.*

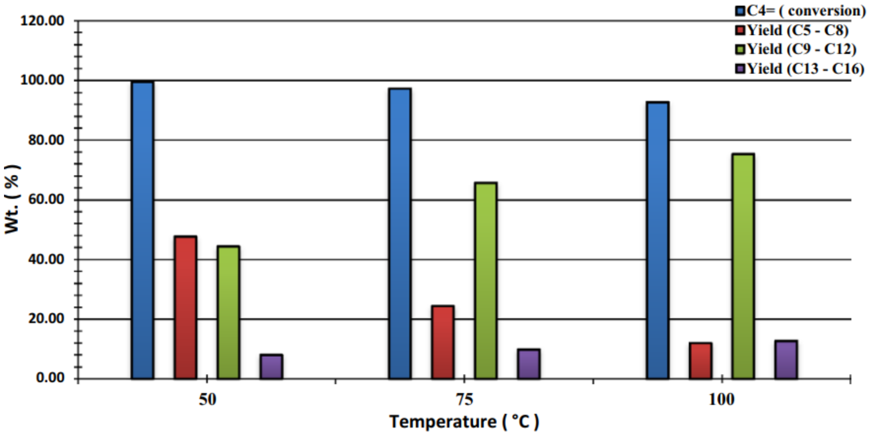


Figure 10. Conversion of C4 and yield of C5-C8, C9-C12 and C13-C16 at different temperatures.

The primary product of the oligomerization reaction was C5-C8 fraction, with a yield of 48% at 50° C. For the C9-C12 fraction, the maximum yield reached was 75% at 100 °C, possibly due to further dimerization of C8 fractions with isobutene. Finally, in the C13-C16 range, the yield was 12%.

Given that supported phosphoric acid on H-Zeolite-Y contains Bronsted acidic sites, it is reasonable to propose that the oligomerization of isobutene progresses through the formation of a tertiary carbenium cation resulting from the addition of H+ to isobutene. Finally, in the C13-C16 range, the yield was 12%.

Finally, Sun et al.[17], synthesized the Fe(NO3)3/β catalyst using mixed C4 fractions as raw materials for the selective oligomerization of isobutylene. Experimental findings indicate that when the loading of the active component was low, there were more acid sites on the catalyst surface, and a higher number of these are necessary for selective oligomerization. The catalyst requires a lower specific surface area, pore volume, and larger pore diameter, which facilitate the reaction of raw materials and the separation of products.

The effects of different active component loadings, reaction temperatures, and reaction space velocities on the reaction were investigated. It was observed that lower active component loadings, lower reaction temperatures, and reduced reaction space velocities promote the occurrence of the desired reaction.

Optimal catalytic performance was achieved at a reaction temperature of 60 °C, reaction pressure of 1 MPa, and reaction space velocity of 1.5 h^−1. Under these conditions, isobutene conversion and selectivities observed were shown in *Figure 11* when different active loadings were used.

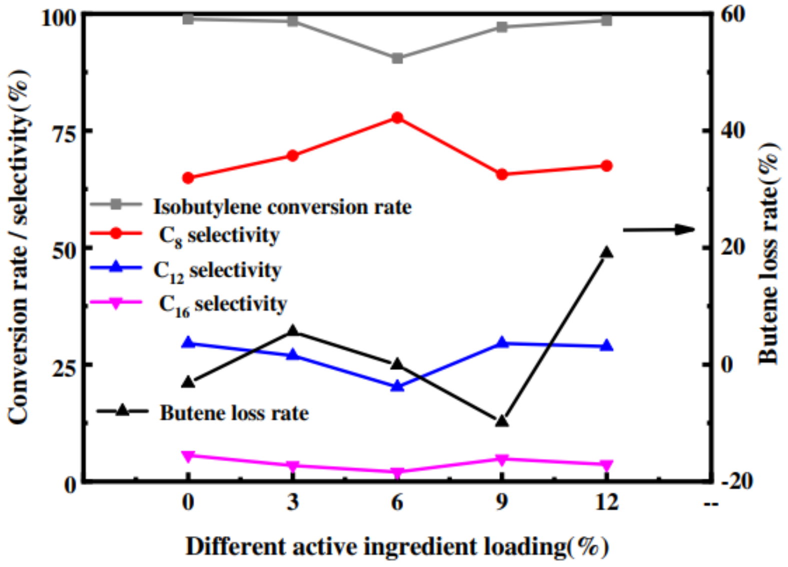


Figure 11. Evaluation results of load sharing among different active components.

As it can be seen, the conversions of isobutanol exceeded the 90% and the selectivity of C8 olefins reached approximately 80%. Regarding C12 chains, the selectivities were around tthe 25% and there was minimal loss of n-butene. Finally, the values of the selectivities obtained from the C16 were very low.

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