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Current uses and trends in catalytic isomerization, alkylation and etherification processes to improve gasoline quality

Review Article

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Abstract: Due to the growing restrictions on the content of aromatic compounds by the European legislation in motor fuels and at the same time the need for higher quality fuels (minimizing the presence of contaminants and hazardous products to health), it has become necessary to increase processes that can maximize the number of octane in gasoline. This manuscript is aimed to provide current trends and processes related to isomerization, alkylation and etherification processes to improve gasolines as final product. Examples provided include the isomerization of light n-alkanes into iso-alkanes or the alkylation, in which the preferred olefin is the methylbutilene and i-butane to produce a high octane number gasoline. Currently, there are two main commercial processes for alkylation processes (hydrofluoric and sulfuric acid technologies). Other incoming suitable process is the etherification of iso-olefins to bio-ethers (the European Union have as a minimum target of biofuel content in fuels of 10% in 2020). The refiners are recently investing in the production of bio-ETBE (ethyl tertiary butyl ether) and other products as additives using bio-ethanol and olefins. Commercial and new potential catalysts for all these processes are currently being used and under investigation.

Keywords: *Gasoline • Isomerization • Alkylation • Etherification • Octane number*

1. Introduction

Due to the increasing regulation of toxic aromatics in motor fuel, there has been a significant demand on processes that can increase the octane number of non-aromatic hydrocarbons [1]. Isomerization processes are used in the refining industry to increase the octane number of light gasolines. This octane number (ON) expresses the resistance to detonation upon fuel combustion in the cylinder in the engine. The practical Octane Number in a gasoline is compared with a theoretical ON 100 provided by isooctane (2, 2, 4-trimethylpentane). Comparatively, pure n-heptane has by definition an ON of 0. The ON of compounds may be higher than 100 because of some of them having better properties than pure isooctane [2]. The isomerization of n-alkanes has been gaining importance due to the restrictions imposed on the use of tetraethyl lead (TEL) as additive in gasolines. This compound is toxic and acts as a catalytic poison for automobile catalytic converters. It was mainly replaced by MTBE (methyl tert-butyl ether) as an additive for ON upgrading. However, this additive has been avoided lately due to its associated contamination of underground waters [3]. The refiners prefer the isomerization of short-chain paraffin like the non-aggressive process for the environment (no lead, tetra-alkylates or carcinogen benzene) to mprove the octane numbers of gasoline. This reaction allows the transformation of n-alkanes (C_4-C_8) which have low octane numbers into iso-alkanes to improve the octane numbers [4]. Catalysts for this purpose are generally bifunctional catalysts. Conventional catalysts for these processes include chlorinated alumina or zeolites (to promote the isomerization) and a metal function for an optimum hydrogenation activity. Typical commercial life-time for these catalysts is 2-3 years depending on the type of catalyst; some of them can be regenerated which increases their lifespan.

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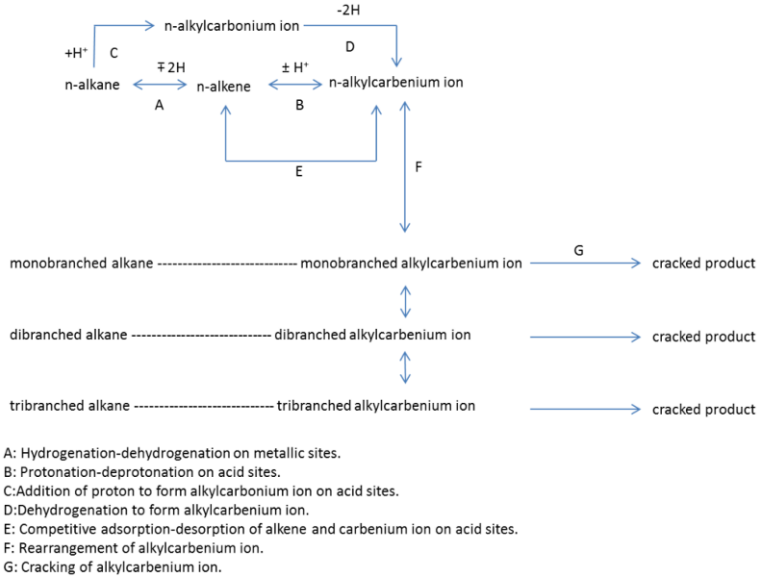


Figure 1. Proposed pathways of hydroisomerization and cracking reactions of n-paraffins by K. C. Park *et al*. in 2001 [9,10].

Trends in the use of etherification reactions (using bio-ethanol) were promoted by the European Union which set a target of 10% minimum biofuel content in fuels by 2020 [5,6]. In this regard, the refiners are mainly investing in the production of bio-ETBE (ethyl tertiary butyl ether) which is produced through the etherification of bio-ethanol and isobutylene.

Finally, the butene alkylation of iso-butane is an important technology to produce gasolines with a high number of multibranched alkanes. Current technologies employ sulfuric acid and HF, which cause environmental and human health concerns. Novel approaches including the use of ionic liquids or solid acid catalysts are currently being investigated in view of a potential future industrial application [7].

1.1. (a) Isomerization, (b) Alkylation and (c) Etherification processes. Introduction and reaction mechanisms

(a) The reaction mechanism of isomerization has been extensively studied. The isomerization process takes place over bifunctional catalysis containing acid (where skeletal isomerization occurs via carbenium ions) and metallic sites (for hydrogenation/dehydrogenation processes) [8]. The dehydrogenation of the paraffin takes place over the metal sites and generates some olefins. These olefins are subsequently protonated on the Brönsted acid sites producing alkylcarbenium ions which undergo structural modifications and a consecutive β-scission, followed by deprotonation and hydrogenation over the metal site to obtain the corresponding product (Fig. 1) [9,10].

Isomerizations are key processes to improve Research Octane Numbers (RON) of the final gasoline. For example, *n*-pentane has a RON of 61.8 and its isomerization product (*i*-pentane) has a RON of 93.5. Comparatively, *n*-hexane RON is 24.8 with respect to 73.4 for 2-methylpentane. The isomerization of *n*-heptane (RON 0) gives products with RON values of 52 (3-methylhexane), 91.1 (2,3-dimethylpentane) and >100 (2,2,3-trimethylbutane). A larger percentage of branched products generally lead to a higher RON in the final gasoline [11].

A classical complete isomerization scheme was proposed by Parera *et. al* [12] for *n*-hexane (Fig. 2).

The hydrocracking reaction is a competing process with hydroisomerization in a bifunctional catalyst. Hydrocracking and coke formation need to be minimized to prevent catalyst deactivation for the production of suitable compounds [13].

(b) The reaction mechanism for Alkylation processes (Scheme 1) involves the formation of a longer-chain highly branched isoparaffin by reacting an alkyl group (almost commercially exclusively isobutene) with a light olefin (mostly butylene) producing a high-octane gasoline. Using propylene and isobutene as raw materials, the alkylation provides a mixture of dimethyl pentane isomers (2, 2 to 2,4). Butylene is the preferred olefin as it leads to the highest RON (ca. 93-95) as compared to propylene (ca. 89-92). This reaction consumes a high amount of propylene and mineral acids (*e.g.* hydrofluoric acid or sulfuric acid) which are employed as catalysts in the reaction. The use of pentene as alkene feedstock provides similar RON

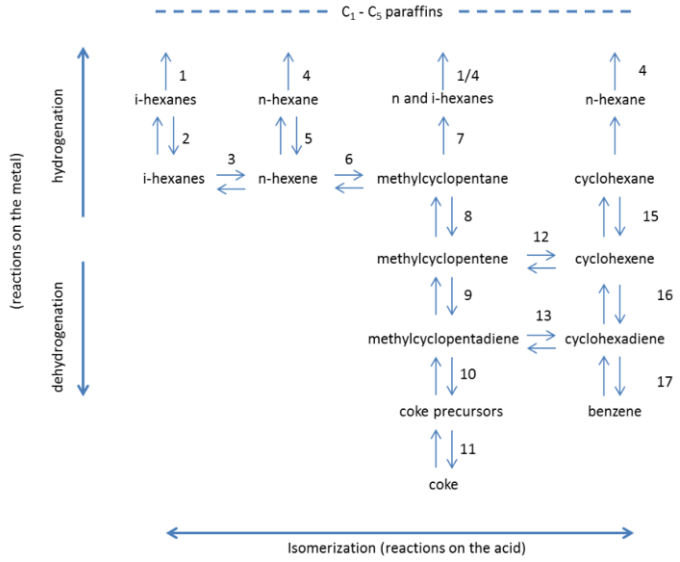


Figure 2. Reaction mechanisms using a bifunctional catalyst (metal-acid/sites) [12].

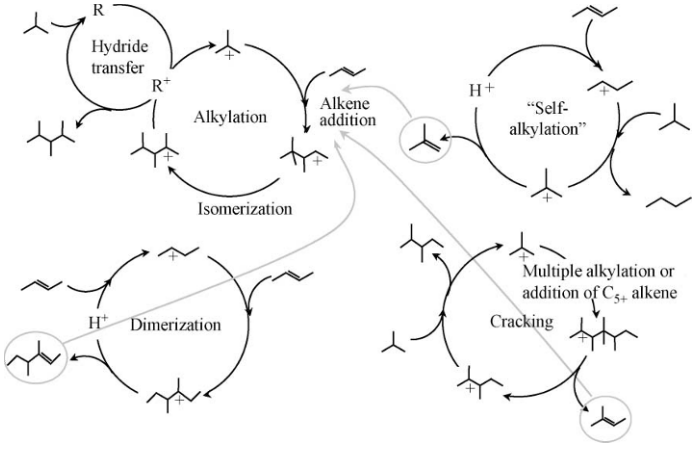
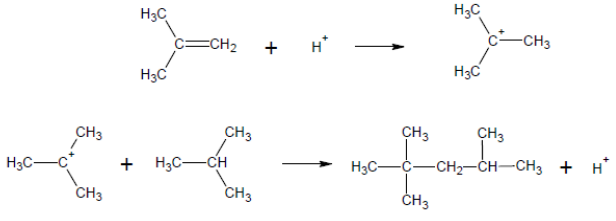


Figure 3. Complete scheme of alkylation reaction [15].



Scheme 1. Scheme reaction for isobutylene and isobutene to form 2,2,4-trimethylpentane (isooctane) [14].

values to those achieved using butylene and propylene but side reactions frequently take place using this olefin as starting material [14].

Feller *et al*. [15] proposed a summary of the complete reaction mechanism in alkylation processes. The alkylation reaction is initiated by the activation of the alkene using mineral acids as catalysts. The alkene reacts to form an ester. In zeolites, the adsorption of an alkene generates an alkoxide over the zeolite surface. These esters may also be converted in free carbenium ions. The tertiary stable cations can be subjected to electrophilic addition to alkene molecules. In a final step, cations are converted into the corresponding alkanes, and the cationic side (catalyst) is regenerated to continue the reaction for both mineral acids and zeolites [15].

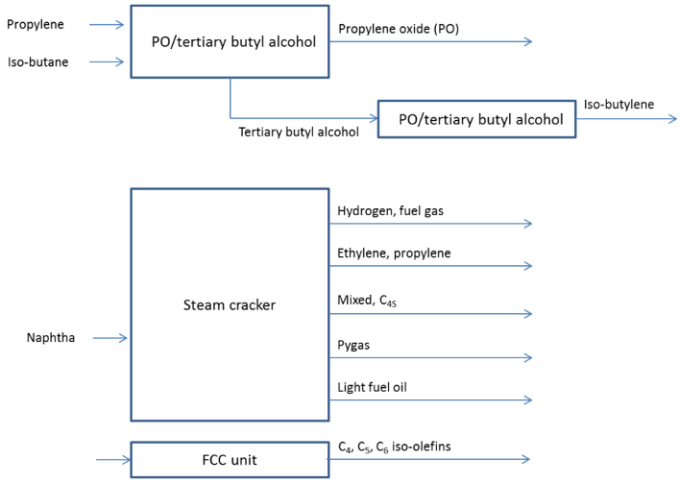


Figure 4. Iso-olefin production in refineries [17].

$(CH_3)_2C=CH_2 + HO\text{-}C_2H_5 / (H^+) \longrightarrow (CH_3)_3\text{-}O\text{-}C_2H_5$

Scheme 2. ETBE formation using ethanol under acid catalysis.

(1) $(CH_3)_3C–OH + R–SO_3–H \leftrightarrow$
$\leftrightarrow (CH3)_3C–O^+H_2 + R–SO_3^-$

(2) $(CH_3)_3C–O^+H_2 + CH_3–CH_2–OH \leftrightarrow$
$\leftrightarrow (CH_3)_3C–O–CH_2–CH_3+H_2O+H^+$

(3) $(CH_3)_3C–O^+H_2 \leftrightarrow CH_2=C(CH_3)_2 + H_2O + H^+$

(4) $R–SO_3^- + H^+ \leftrightarrow R–SO_3–H$

Scheme 3. ETBE production using an acidic resin as catalyst [16].

(c) The etherification mechanism is similar to that represented in Scheme 1, but in this case an alcohol (*e.g.* ethanol) is employed as substrate in acid medium. A cation exchange resin has been typically employed as a catalyst. Scheme 2 illustrates an example for the production of Ethyl tert-butyl ether [17].

ETBE was also produced by using a polymeric ion exchange resin catalyst from ethanol and tert-butyl alcohol [16].

The investment cost to produce bio-ETBE is very low because existing MTBE units can be used for the production of ETBE [17]. Bio-ETBE is a stable additive which reduces final vapor pressure in gasolines as compared to the use of pure bioethanol. Bioethanol blends can lead to problems in engines due to the hygroscopic character of ethanol (less stable than ETBE as additive for gasolines). Nevertheless, a 5% bioethanol blend entails a ca. 4.3 points RON increase as compared to an increase in 2.3 points for the addition of a 15% of ETBE or TAEE (tertiary amyl ethyl ether) [17,18].

Many refineries have iso-olefins available in sufficient quantities,and in this case it will be possible to use a similar technology to that utilized for MTBE production, with significant opportunities for the petrochemical industry. Final high-octane bioethers with low vapor pressure can also be added to the gasoline. Some examples of sources (iso-olefins) are summarized in Fig. 4.

Not only can bio-ETBE be produced in refineries, tertiary amyl ethyl ether or other heavy bio-ethers can also be produced using the same procedure.

One more example of synthesis different from ETBE is the tertiary amyl ethyl ether synthesis. The scheme reaction for TAEE is depicted in Fig. 5 [19].

2. Technologies and catalysts

2.1. Catalysts for light paraffin (C5-C6) isomerization

There are 3 types of isomerization processes. High temperature processes (360 – 440°C) are generally promoted by fluorinated alumina. Medium temperature reactions (250 – 300°C) have been reported to be promoted using zeolites while chlorinated alumina is utilized at low temperatures (120-180)°C. $Pt/ZrO_2\text{-}SO_4$ catalysts are widely employed in industry in processes at 130-180°C.

Fig. 6 summarizes a typical evolution of the isomerization-reaction (content of i-C5/C5, % *vs.* temperature, °C) using different catalysts.

(a) Catalysts $Pt/Al_2O_3\text{-}Cl$

These catalysts are based on chlorinated alumina. Compared with other types of used catalysts in this process, they are the most active and provide the

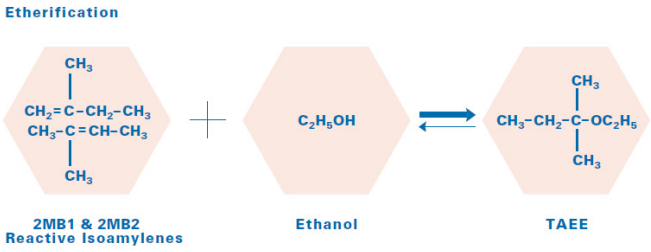


Figure 5. TAEE formation [19].

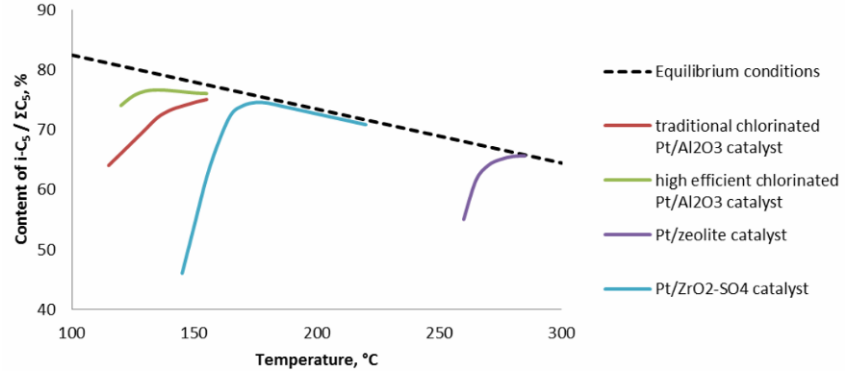


Figure 6. Comaprative activity of differently used catalysts in the industry [20].

greatest yields to isoalkanes, thus isomers with the highest octane number.

This reaction needs the addition of alkyl chlorides to the feed, due to the gradual reduction of acidity in the isomerization catalyst during the process (which decreases isomerization activity). The reactor is affected by the deposition of some products from these alkyl chlorides which need to be removed. Additional issues include a high sensitivity to nitrogen, sulfur, benzene and water which can poison the catalysts. Often the feedstock needs to be purified, making the process more expensive. Main manufacturers of these catalysts are UOP (I-82, I-84) and Axens (ATIS-2L) [20,21].

(b)Zeolites

Zeolite catalysts are comparably less active than chlorinated alumina and therefore require higher operating temperatures with respect to other types of catalysts. These catalysts, however, possess a high resistance to impurities in the feed and they can be regenerated more easily (directly in the reactor) as compared to chlorinated catalysts. The molar ratio of hydrogen to hydrocarbons used for the process is higher with these catalysts compared to those used for chlorinated alumina. Due to their high molar ratio hydrogen/hydrocarbons, it is necessary to recycle the hydrogen in this process requiring a compressor and separator. Main foreign licensors of processes with zeolites are companies UOP (HS-10 catalyst), Axens (IP-632), Süd Chemie (Hysopar) and JSC SIE Neftehim (SI-1) [20,21].

(c) Pt/ZrO_2-SO_4

These catalysts demonstrate good properties and activity for the isomerization processes. They are resistant to catalyst poisoning and they can be regenerated in a similar way to those of zeolite catalysts (21). Temperature stability (only up to 650ºC, with problems often arising at 400ºC) is the main drawback of these types of catalysts. Some commercial materials include UOP (LPI-100, PI-242) and Russian JSC SIE Neftehim (SI-2) [21].

Tables 1a, 1b and 1c summarize the different commercial reaction-conditions used for each type of catalyst and the obtained octane numbers for gasoline upon isomerization.

(d)Heteropoly Acids (HPAs)

HPAs are complex proton acids consisting on polyoxometalate anions in which the basic structural unit metal-bond-oxygen is in an octahedral form [22]. They have strong Brönsted acidity which is useful in isomerization reactions. There are some commercially available catalysts including $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$.

Kuang *et al*. [23] evaluated the effect of HPW content in the catalyst structure and reactivity of samples HPW/SiO_2. They carried out the isomerization of n-hexane at 225°C. Upon mixing silica in a HPW mass with

Table 1a. Performances of zeolite catalysts, yields, obtained Research Octane Numbers [21].

Performances of UOP, Axens, Süd Chemie and JSC „NPP Neftehim“ isomerization technologies (RON of the feed = 70-73)				
Parameter	**Pt/zeolite**			
	UOP Zeolitic Process HS-10	Axens IP-632	CKS Süd Chemie CKS ISOM Hysopar	JSC NPP Neftehim Izomalk-1 Сж-1
Temperature, °C	260-280	250-270	240-280	250-270
Pressure, MPa	1.5-3.0	1.5-3.0	3-3.2	2.5
LHSV, h^{-1}	2	1-2	2	2
Mole ratio H_2:CH	4:1	(3-4):1	1.6:1[3]	-
Compressor	Is necessary			
Chlorine compound injection and caustic soda washing	Absent			
Impurities in the feed:			-	-
- H_2O, ppm	50 (200)[1]	50 (200)[1]	≤ 200	10-20 MT m^{-3}
- nitrogen, ppm	1	1	-	-
- sulfur, ppm	50 (100)[1]	50 (100)[1]	100(200)[1]	≤ 1
- benzene, % wt.	5 (15)[1]	5 (15)[1]	-	-
-C7+, % wt.	2-3	2-3	-	-
Service cycle (lifetime)	2-3 years (10 years)			
RON, points		-	-	-
- “one-through”	78-80	80	78-80	80
- with DIP (DIP and DP)[4]	-	82	80-83	-
- with DIH	-	86	-	82-85
- with DIP and DIH	-	-	-	-
- with DIP, DIH and DP	-	-	-	-
-with n-C_5, n-C_6 recycle on the molecular sieves	87-90 (TIP)	88 Ipsorb 90 Hexorb[5]	-	-
Yield of isomerization, % vol.	97-98	---	98.1	-
$iC_5/\Sigma C_5$, % wt.	53-62			
2,2-DMB/ΣC_5, % wt.	10-16			

Table 1b. Performances of Pt/chlorinated Al_2O_3 catalysts, yields, obtained Research Octane Numbers [21].

Performances of UOP, Axens, Süd Chemie and JSC „NPP Neftehim“ isomerization technologies (RON of the feed = 70-73)		
Parameter	**Pt/chlorinated Al_2O_3**	
	UOP Penex I-8 Plus, I-82, I-84	Axens IS 614 A (ATIS-2L)[2]
Temperature, °C	120-180	120-180 (110-170)
Pressure, MPa	3.0-4.0	2
LHSV, h^{-1}	1.5	2
Mole ratio H_2:CH	(0.3-0.5):1	< 1
Compressor	Absent	
Chlorine compound injection and caustic soda washing	Is necessary	
Impurities in the feed:		
- H2O, ppm	0.1	0.1
- nitrogen, ppm	0.1	0.1
- sulfur, ppm	0.1-0.5	0.1-0.5
- benzene, % wt.	≤ 1	≤ 1
-C7+, % wt.	< 1	≤ 1
Service cycle (lifetime)	-	IS 614 is capable of regeneration
RON, points		
- “one-through”	83-86	83 (84-85}
- with DIP (DIP and DP)[4]	-	84 (85-86)
- with DIH	87-90 (Penex / DIH)	88 (89-90)
- with DIP and DIH	90-93 (DIP-Penex / DIH)	-
- with DIP, DIH and DP	-	-
-with n-C_5, n-C_6 recycle on the molecular sieves	88-91 (Penex / Molex)	90 (90-91) Ipsorb 92 (92-93) Hexorb[5]
Yield of isomerization, % vol.	≥ 99	-
$iC_5/\Sigma C_5$, % wt.	70-78	
2,2-DMB/ΣC_5, % wt.	30-36	

Table 1c. Performances of sulfated zirconia catalysts, yields, obtained Research Octane Numbers [21].

Performances of UOP, Axens, Süd Chemie and JSC „NPP Neftehim" isomerization technologies (RON of the feed = 70-73)		
Parameter	**Pt/ZrO_2-SO_4**	
	UOP Par Isom	JSC NPP Neftehim Izomalk-2
	PI-242	Сж-2
Temperature, °C	140-190	120-160
Pressure, MPa	3.2	2.5-2.8
LHSV, h^{-1}	2.5	2.5-3.5
Mole ratio H_2:CH	2:1	(1.5-2.5):1
Compressor	Is necessary	
Chlorine compound injection and caustic soda washing	Absent	
Impurities in the feed:		
- H2O, ppm	≤ 20	≤ 20
- nitrogen, ppm	1	1
- sulfur, ppm	1-5	2-5 (50)[1]
- benzene, % wt.	≤ 10	≤ 10
-C7+, % wt.	≤ 5	≤ 5
Service cycle (lifetime)	2-3 years with pretreatment (8-10 years)	
RON, points		
- "one-through"	81-83	82-84
- with DIP (DIP and DP)[4]	-	85-86[4]
- with DIH	86-87 (Par-Isom / DIH)	87-89
- with DIP and DIH	-	89-90
- with DIP, DIH and DP	-	91-92
-with n-C_5, n-C_6 recycle on the molecular sieves		91-92
Yield of isomerization, % vol.	≥ 97	97-98
$iC_5/\Sigma C_5$, % wt.	68-72	70-75
2,2-DMB/ΣC_5, % wt.	20-27	28-34

[1] – at short times;
[2] – data for ATIS-2L catalyst are in brackets;
[3] – according to data of Angarsky Refinery;
[4] – data for scheme with C_5 recycle (DIP and DP);
[5] – process with C_5, C_6 and methylpentanes recycling.

Pt/Al_2O_3 at a 1: 1 ratio, the selectivity of the isomerization products (from 98.9 to 99.5%) was improved and the conversion of n-hexane was remarkably increased [23].

(e) Mesoporous materials.

Controlled porosity development in materials that include silica and activated carbon in view of their catalytic applications has been an alternative area of great scientific and technological interest in recent years [24]. The design of materials with controlled pore size and shape is important, particularly in applications where a molecular recognition is needed: molecular sieves, chemical sensors, adsorbents and especially selective catalysts. Mesoporous catalysts made of sulfated zirconia supported by MCM-41 were recently developed and are significantly active with i-C_5 which is used in the isomerization of n-pentane [25]. Unfortunately catalysts including MCM-41 materials are not stable at high pressures and they do not have sufficient acidity to promote isomerization reactions as compared to microporous materials (*e.g.* zeolites, chlorinated alumina and metal oxides).

(f) Sulfonated resins.

Sulfonated resins are generally applied isomerization catalysts. The catalyst is usually composed of sulfonated polystyrene (copolymer of styrene and divinylbenzene) or sulphated phenol-formaldehyde copolymer. In 1964, a process for the isomerization of olefins C_4-C_6 using these types of catalysts was patented [26]. Olefins isomerization is carried out at moderate temperatures (about 100°C) and pressures and reaches a high selectivity and yield to isomers [27]. A sulfonated macroporous poly(styrene-divinylbenzene) catalyst was later employed in the isomerization of n-butane which experienced fast deactivation [28].

(g) Pt/WO_3-ZrO_2 (PtWZr).

Pt/WO_3-ZrO_2 catalysts have shown interest in the isomerization of light and heavy paraffinic feedstocks. These catalysts have high activity and selectivity for alkane skeletal isomerization, a highly relevant process for the production of high quality gasolines [29]. These catalysts currently constitute an interesting alternative option in producing high-quality clean fuels in view of the environmental concerns in the European Union [30]. Anisia *et al*. reported interesting results in the PtWZr catalyzed isomerization-cracking reaction using heavy raw materials (long chain paraffins) [4]. These catalysts were also proposed to obtain adequate light products from Fischer-Tropsch wax (Sasol H1 as raw material)

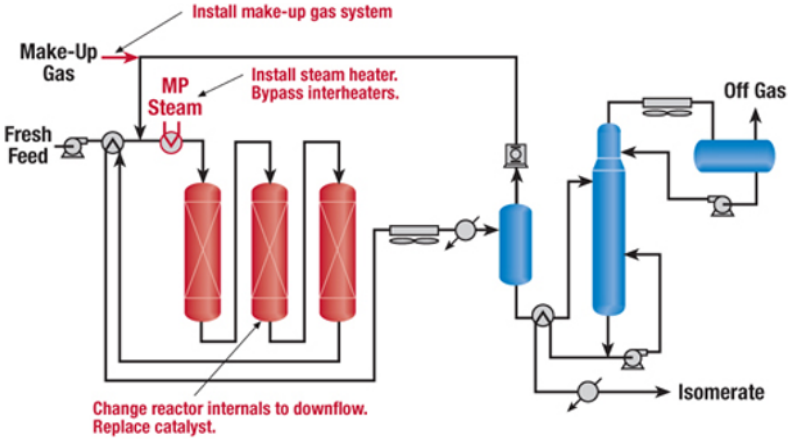


Figure 7. Par. Isom. Process by UOP.

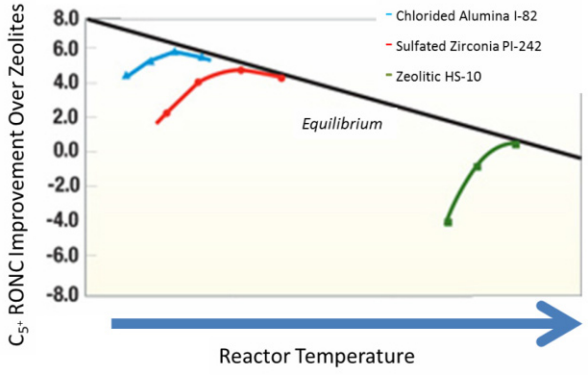


Figure 8. Activity *vs.* temperature for different commercial catalysts from UOP LCC.

having a 50 wt.% selectivity to diesel fuel. Literature data indicates the need of adding a promoter or a second support or active species to these materials to improve their activities (as compared with commercial catalysts). The addition of some SO_4-ZrO_2, WO_3-ZrO_2 or zeolites to the initial composition of PtWZr could thus be beneficial. Ying *et al.* [1] proposed the use of Pt/WO_3/Al ZrO_x as a highly active and selective nanocomposite catalyst for C_{7+} paraffin isomerization. This type of catalyst was developed to improve results from traditional catalysts such as platinum chlorinated alumina in order to minimize pollution and environmental issues generated in the production of final commercial gasolines.

(h) Molybdenum Oxide based Catalysts

These types of catalysts exhibit a high resistance to sulfur and nitrogen poison present in the used feedstock. They have been used for short and long chain paraffin isomerization (n-butane, n-pentane, n-octane). Reported studies found a high selectivity to isomers [22]. The active phase in these materials was proposed to be related to a Mo_2C or some oxy-carbide of a MoO_xC_y in the isomerization of light paraffins [31].

2.1.1. Commercial processes for light paraffin isomerization

Some commercial catalysts detailed in section 2.1 are currently employed worldwide. Processes used in industry (produced by the bigger licensers) today can be summarized as follows:

(a) Axens proposes the catalyst (chlorinated alumina) ATIS 2L in its isomerization process. The **Ipsorb Isom Process** uses a de-isopentanizer to separate isopentane from the reactor feed. A small amount of hydrogen is also added to the feed. The catalyst has a long service life. Reactor products are separated into isomers and normal paraffins in the Ipsorb molecular sieve separation unit which features a vapor phase PSA technique. This enables the product to be consistently comprised of branched isomers [32].

An Octane Number (ON) of 92 from 75 (parent feedstock) can be obtained using this process.

(b) **Par Isom Process.** UOP LLC licensed a process capable to obtain a product with an ON of 87. Ten units of this process were in operation in 2004. The process makes use of PI-242 (sulfated zirconia). The feed is combined with made-up and recycled hydrogen which is directed to a pre-heater and into the reactor. The stabilized isomerate product can be directly sent to gasoline blending.

UOP has not only a “chlorinated alumina” catalyst type (Fig. 8) in their portfolio:

Another process is the HOT (hydrogen-one-through) Penex process (UOP LCC) which uses highly active advanced isomerization catalysts without the need for a recycled gas compressor.

(c) Neftehim isomerization processes

Additional relevant information is provided by the Neftehim company. This company is the Licensor of isomerization processes over zeolite catalyst (SI-1,

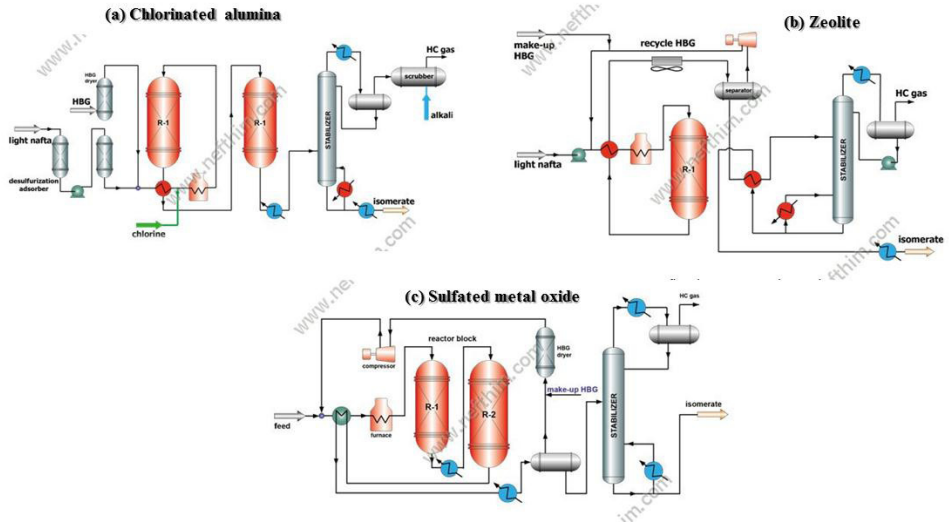


Figure 9. Neftehim technology for C5-C6 paraffins isomerization processes.

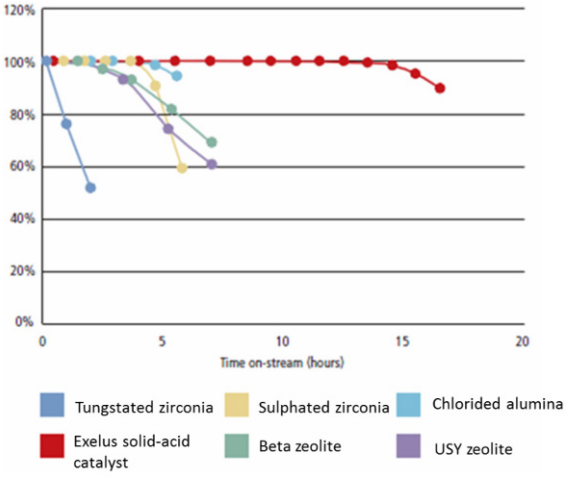


Figure 10. Different obtained yields using different solid heterogeneous catalysts of isobutane and 2-butene [33].

Isomalk-1) and sulfated zirconia (SI-2, Isomalk-2). Comparative data on different isomerization catalysts are given by Neftehim on Fig. 9.

The chlorinated alumina-mediated process needs a scrubber to eliminate the organic compounds. The catalyst has a normal life of 3-5 years, but it cannot be regenerated. Comparatively, the process using zeolite produces low octane products (7678) and it needs a hydrogen-bearing gas (HBG) recycler, while the analogous with sulfated zirconia, uses a HBG dryer and a compressor to recover hydrogen.

2.2. Catalysts for the alkylation process

Current technologies use hydrofluoric or sulfuric acid as catalysts, but these mineral acids are hazardous and the processes are very environmentally unfriendly. Research and applications attempting to substitute these liquid acids by other acid solids are currently ongoing.

Mukherjee *et al*. [33] showed different catalytic activities using their own commercial solid acid catalyst "Exelus" (Fig. 10), obtaining optimum results in the alkylation of isobutane and 2-butene.

Tungstated zirconia, sulphated zirconia, chlorinated alumina, beta zeolite and USY zeolite are obvious alternatives in the alkylation process conducted under identical conditions for all the catalysts, exclusively changing the temperature (20-30°C for zirconia catalysts and alumina and 70-90°C for zeolites) [34].

An integrated alkylation-isomerization process using solid catalyst for isomerization is claimed in US patent 7,439,410 B1 [34], similar to that of catalysts depicted in Fig. 10. A chlorinated organic promoter (*e.g*. chlorinated paraffins) was also employed to promote the alkylation.

Some zeolite-promoted technologies available include the Exelus ExSact process (Fig. 10) [35], and the ABB Lummus Alkyclean process [36]. Other different mesoporous functionalized Nafion/SBA-15-based catalysts have been reported in the alkylation of isobutane/1-butene [37].

2.2.1. Commercial processes for alkylation

Sulfuric acid and HF acid-promoted catalysis comprise the main technologies currently used for alkylation. The reaction with sulfuric acid requires cooling of the reaction mixture while HF-promoted alkylations can operate under cooling water temperatures. The most extended process utilizes sulfuric acid as HF is highly hazardous. An excess of isobutane is normally required

Table 2. Selected commercial technologies for the alkylation process.

Provider	Features
CDTECH (1)	CDAlkyl low temperature sulfuric acid alkylation.
CDTECH (2)	CDAlkylPlus low temperature sulfuric acid alkylation coupled with olefin pretreatment step.
DuPont	Uses STRATCO Effluent Refrigeration Alkylation process using sulfuric acid.
Lummus Technology	AlkylClean process using solid acid catalyst. Demonstration unit only.
Refining Hydrocarbon Technologies LLC	RHT-Alkylation process uses sulfuric acid. Eductor mixing device.
ExxonMobil Research and Engineering	Sulfuric acid alkylation using auto-refrigerated reactor.
UOP (1)	Modified HF Alkylation to reduce aerosol formation.
UOP (2)	Indirect Alkylation (InAlk) uses solid catalyst. Olefins polymerize and higher molecular weight material hydrogenated.
AXENS	APC - HF Alkylation
ALBEMARLE	ALKYCLEAN. Using a zeolite as solid catalyst.

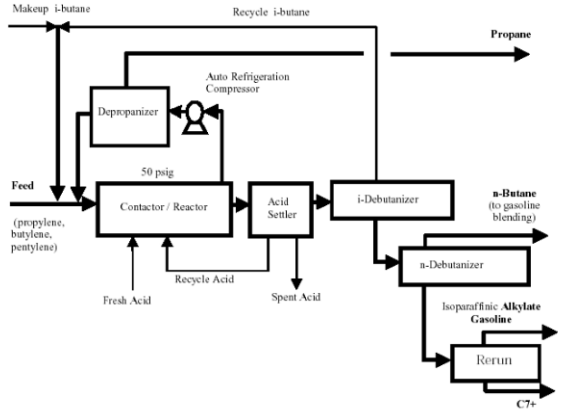


Figure 11. Sulfuric Acid catalyzed Alkylations [38].

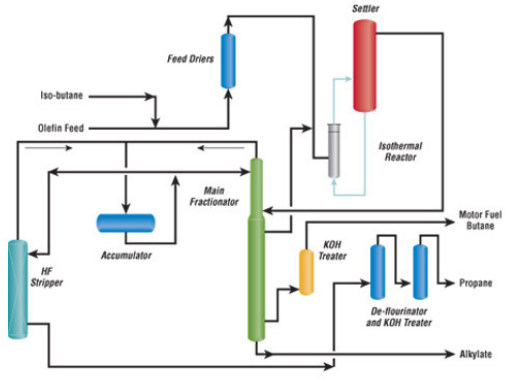


Figure 12. Scheme for HF alkylation process by UOP.

in such reactions, with a volume ratio of isobutane to olefin of 3-12. Newer plants have multi-injection and vigorous mixing systems, depicting isobutane to olefin ratios of 10,000 to 1 [14].

Fig. 11 illustrates the alkylation reaction using sulfuric acid as a catalyst. The feed containing the respective olefin is mixed in the reactor with the fresh acid producing the new high "octane number product" and other secondary products (*e.g.* propane) which can be removed. During the process, i-butane and the acid (Fig. 11) are continuously recycled to maximize feedstock conversion. The principal product is the isoparaffinic alkylate gasoline with a high octane number.

Table 2 summarizes some of the used commercial technologies in companies including "CDAlkyl low temperature sulfuric acid alkylation" by CDTECH (using sulfuric acid) or the "Modified HF alkylation to reduce aerosol formation" by UOP (using hydrofluoric acid).

The UOP alkylation process comparably uses HF as an acid catalyst (Fig. 12). In this case, the presence of HF needs to be omitted in the final product. The feedstock (iso-butane and the olefin) is mixed and heated to the adequate temperature in the isothermal reactor and then sent to the main fractionator in which HF and the different products are separated. The alkylate compound is the primary product. Butane and propane are produced as secondary products (necessitates the presence of an HF treatment unit to separate this gas).

2.3. Potential and commercial catalysts in paraffin etherification for bio-ether production

Commercial cation exchange resin, acidic resin catalysts are generally used in etherification reactions between C_4 and C_5 iso-olefins and alcohols. Heteropoly acid compounds are currently under investigation as potential catalysts in the production of tertiary ethers.

Ancillotti and Fattore reviewed the used catalyst for etherification in 1998 [39]. The commercial

Table 3. Comparison of resin performance in MTBE preparation.

	Resin type	Surface area (m^2/g)	Catalytic sites on surface (%)	Isobutene conversion to MTBE at 60°C (%)
Amberlyst 15	Macroreticular	55	< 4	95
Amberlyst XN1010	Macroreticular	615	about 50	79
Amberlite IR 132C	Gel	--	--	30

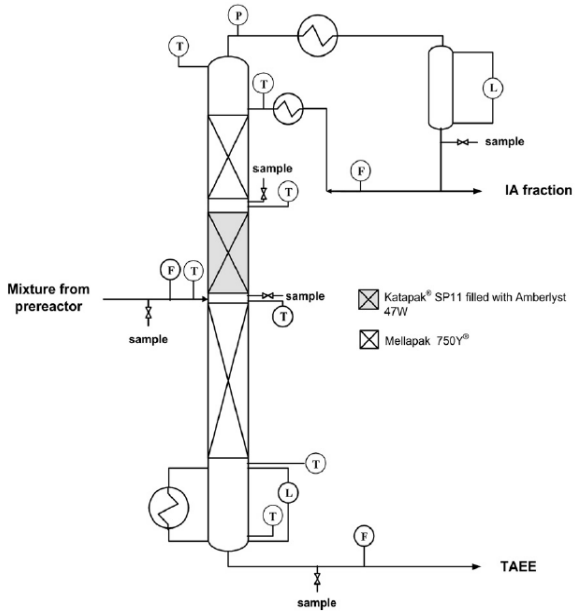


Figure 13. Experimental setup for TAEE synthesis from EtOH and FCC gasoline. F (flow), P (pressure), T (temperature), L (liquid tank level) [40].

catalyst (Amberlyst-15) is a macroreticular sulfonic resin manufactured by Rohm and Haas; a sulfonated copolymer of styrene and divinylbenzene [40]. For further reading on this topic, readers are referred to the recent review on the topic by Yee *et al*. [41], mostly related to ETBE production, history and future prospects. They compared ETBE and MTBE properties. ETBE had a higher octane number, boiling point and lower solubility in water and was significantly less toxic. Kiatkittipong *et al.* [42] proposed the etherification of FCC gasoline using glycerol to obtain a higher RON in the final product. They studied the activity of Amberlyst 15 and 16 as well as a beta-zeolite to obtain Amberlyst 15 as an optimum catalyst for the reaction. The production of ETBE was achieved in great yields also using silicotungstic acid and tungstophosphoric acid catalysts calcined at different temperatures [43]. Comparatively, Amberlyst 47 W ion exchange resin provided a yield of 24% molar of TAEE [44]. Fig. 13 illustrates the used equipment for TAEE production.

Montmorillonites or bentonites are potential alternative catalysts. They are generally less active as compared to commercial resins but also cheaper [45].

Chu and Kuhl [46] utilized ZSM-5 and ZSM-11 zeolites in liquid phase reaction and made a comparison with Amberlyst-15 obtaining similar results. The authors claimed a higher thermal stability, regenerability by calcination, low sensitivity to methanol/isobutene ratio and higher productivity of zeolites with respect to commercial catalysts.

Table 3 summarizes the obtained MTBE yields using different commercial catalysts.

3. Conclusions

There is an increasing need to design environmentally friendly systems compatible with the discussed processes to improve the quality of final gasoline products. These need to be in agreement with current legislation and society requirements. Due to the growing need in society for fuels and the gradual increase in components such as sulfur, nitrogen, metals and other compounds in the oil (which negatively affect catalysts), research relating to the use of novel catalysts should be enforced as there is an increasing commercial interest. An increase in the addition of biofuels to gasoline is expected in the near future (promoted by legislation and the needs of alternative fuels thus favoring etherification processes in which bio-ethanol could be added a bio-additive, avoiding the use of MTBE (compound considered as carcinogen). Alkylation processes are also highly attractive as they allow the possibility to synthesize a clean gasoline without contaminants and a high octane number. End products can be directly used as an additive or as high octane gasoline. The discussed processes can be a solution already available and used in refineries worldwide for future development with more sustainable practices.

Current trends in industry intend to replace classical techniques by more advanced, cheaper and environmentally friendly methodologies.

Catalytic isomerization processes will be aimed to replace chlorinated alumina by other less corrosive materials, less polluting and less sensitive to impurities, related to the use of ZrO_2 -SO_4 and zeolites as well as ongoing research on new materials such as mesoporous materials, new zeolites, Mo materials or catalysts with promising studies (*e.g.* Pt/WO_3-ZrO_2).

Industrial attempts in the field of gasoline additives (already a fact replacing the tetraethyl lead) replace MTBE by ETBE and bioethanol addition (in blends). Direct alkylation of synthetic gasolines with a higher octane number (*e.g.* isooctane obtained by the reaction between isobutane and isobutene has a RON of 100) is another alternative depending on the number of side reactions. In the latter case, the use of hazardous and corrosive acids such as HF or sulfuric acid is aimed to be replaced by another type of environmentally sound catalysts including zeolites or sulfonated resins (Amberlyst-15 commercial catalyst). These materials are safer and can often provide a more selective route to suitable products.

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