

# Catalytic Processes for the Production of Automotive Gasoline

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Edited by Heriberto Díaz Velázquez

First published 2025

ISBN: 978-1-032-84435-0 (hbk)

ISBN: 978-1-032-89071-5 (pbk)

ISBN: 978-1-003-51728-3 (ebk)

## Chapter 5

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### Alkylate Gasoline

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DOI: 10.1201/9781003517283-5

The funder of the Open Access version of this chapter is Consejo Nacional de Humanidades, Ciencia y Tecnología (CONAHCyT) (project number CF-191973), and Mexican Petroleum Institute (project number Y.62011)



**CRC Press**

Taylor & Francis Group

Boca Raton London New York

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# 5 Alkylate Gasoline

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## 5.1 INTRODUCTION

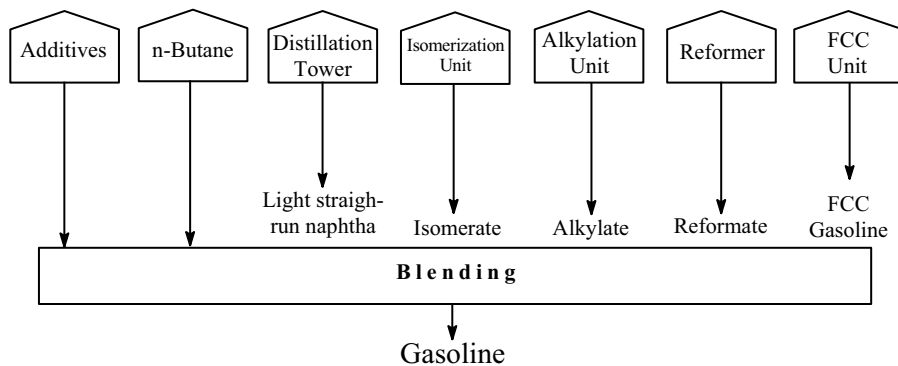
The transportation of goods and people worldwide is an energy-intensive activity that mainly involves light and freight vehicles<sup>1</sup> and is correlated with population growth and the access of societies to more consumer goods. Its increase is expected to be more pronounced in non-OECD (Organization for Economic Co-operation and Development) countries, mainly India and China, reaching 2 billion light-duty cars and almost 800 million freight vehicles globally by 2040. From 2025 to 2040, air travel is projected to be the fastest-growing means of transportation, which is highly dependent on gross domestic product (GDP) growth.<sup>2</sup> It is estimated that 20% of the consumed energy corresponds to transportation and contributes to 14% of greenhouse gases (GHGs).<sup>3</sup> On the other hand, approximately 80% of cars use spark ignition engines. In contrast, diesel engines predominate in the commercial sector,<sup>4</sup> and so about 60% of crude oil is used to make transport fuels, of which almost 5 billion liters per day correspond to gasoline.<sup>5,6</sup> In this context, in many countries, stricter legislation, including fuel taxes, carbon emission taxes, and subsidies for renewable energies, has been implemented to reduce pollutant emissions.<sup>7,8</sup>

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**TABLE 5.1**  
**Properties of Industrial Liquid Acid Catalysts**

Properties	HF	H <sub>2</sub> SO <sub>4</sub>
Molecular weight, g/gmol	20.0	98.08
Density, g/mL	1.002 (4 °C)	1.8 (20 °C)
Boiling point, °C (760 mm Hg)	19.5	290
Freezing point, °C	-83	10.31
Vapor pressure, mm Hg	917 (25 °C)	1 (146 °C)
Viscosity, cP	0.256 (0 °C)	33 (15 °C) (21 mPa.s (25 °C))
Surface tension, mN/m	10.2 (0 °C)	51.7 (50 °C)
Specific heat, Btu/lb/°F	0.83 (-1 °C)	0.33 (20 °C)
Hammet acidity (-H <sub>0</sub> ), 25 °C	10.0	11.1
Dielectric constant	84 (0 °C)	114 (20 °C)

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**FIGURE 5.1** General outline of gasoline production.

Gasoline is a complex mixture of hydrocarbons that also depends on the time and place where it is produced<sup>8</sup> and involves the use of different and complex technologies to produce it as shown in Figure 5.1.<sup>9</sup> It is a volatile and flammable mixture of hydrocarbons obtained mainly from petroleum refining.<sup>10</sup> The gasoline pool is composed of streams coming from different units, including straight-run naphtha, isomerate, reformate, alkylate, fluidized catalytic cracking (FCC), hydrocracked naphtha, and polymer gasoline,<sup>11,12</sup> and contains compounds such as alkanes (paraffins), isoalkanes (isoparaffins), olefins, naphthenes, and aromatics, known as PIONA.<sup>13</sup> Gasoline consists of different proportions of these streams, and other special additives must meet ecological and quality requirements to function appropriately in engines and, consequently, generate low exhaust emissions. Therefore, the composition and properties of fuels are guided by legal provisions.<sup>14</sup> The streams that makeup gasoline are at boiling points ranging from  $-20$  to  $230$  °C, and its components have a carbon number distribution between C4 and C12. An accelerated decrease in gasoline demand is expected, mainly in OECD countries due to the implementation of decarbonization and technologies with lower CO<sub>2</sub> emissions; in contrast, developing countries still show a tendency to increase consumption until 2050 because they are societies that do not have a saturated automotive market. However, in developed countries, the number of cars per 1000 inhabitants has displayed a constant trend (e.g., in the USA, 838 and 836 in 2008 and 2018, respectively), but in developing countries, the number of cars per 1000 inhabitants has a wide margin to grow (e.g., India 13.2 and 43.6, China 35.7 and 167, or Mexico 230.2 and 343, for the years 2008 and 2018, respectively).<sup>8,11,15</sup>

As for cars, knocking in gasoline engines is caused by the rapid combustion of an air–fuel mixture that does not burn in the regular flame front. When air is compressed with gasoline, the latter has to self-ignite before the ignition spark, thus creating resistance to the engine compression stroke, which is known as knocking. Moreover, adequate engine fuel efficiency is an essential characteristic. In this context, the anti-knock performance is measured from the octane number (ON), which is one of the essential properties of gasoline and probably the most recognized measurement of the quality of gasoline and is defined as the volume percentage of *i*-octane in a

mixture of *n*-heptane and *i*-octane.<sup>16</sup> There are two ASTM methods for measuring this index: the Research Octane Number (RON, ASTM D2699) and the Motor Octane Number (MON, ASTM D2700). Always RON > MON, and the difference between them is known as gasoline sensitivity.<sup>17</sup> Historically, the ON has been increased to decrease the antiknock performance. Sulfur and nitrogen, among others, have been decreased to reduce the environmental impact of the output emissions, which considerably decreased the contents of hydrocarbons, CO, NO<sub>x</sub>, SO<sub>x</sub>, and particulate materials, whereas the presence of oxygenated compounds has been increased.<sup>12,18</sup> From the point of view of using fuels from nonrenewable sources, not only the gasoline pool has been improved but also the efficiency of the engines has decreased due to the impact of emissions and increasing digitalization.<sup>19</sup> Car manufacturing companies have developed and employed technologies aimed at reducing specific fuel consumption in engines and achieving greater efficiency<sup>6,20</sup> that include continuously variable transmission, cylinder deactivation, start-stop systems, variable valve timing, direct fuel injection, and turbocharging technologies.<sup>8</sup> The use of electronic control generated the possibility of increasing the compression ratio of engines (from 8 in 1970 to 9.5 in 2005), which resulted in less-polluting exhaust gases that allowed the implementation of Euro and Tier standards.<sup>8</sup>

Alkylation is an essential refining process for producing higher-quality gasoline and meeting increasingly stringent standards for air quality, carbon emissions, and automotive efficiency. Due to alkylation, carbon emissions have been decreased by half, and emissions of air pollutants have fallen by 80% since the 1970s.<sup>21</sup> The combination of the different streams that make up the gasoline pool (Figure 5.1) and other components, such as ethanol, made it possible to increase the octane rating, which has helped the engine performance achieve lower GHG emissions. Alkylate provides other attributes that reduce environmental pollution such as low volatility and low evaporative emissions, resulting in low Reid vapor pressure (RVP), high RON and MON values, and no aromatic or sulfur compounds.<sup>10</sup> Because of the above characteristics, the demand for the contribution of the other streams to the gasoline pool was reduced, except for the alkylate.<sup>22</sup>

The development of the alkylation reaction dates back to the 1930s when companies such as UOP, Shell, Anglo Iranian Oil Company, and Texaco made public alkylate obtainments. The employed catalysts were combinations of strong Lewis acids (AlCl<sub>3</sub> or BF<sub>3</sub>) with acids such as HCl or hydrofluoric acid (HF).<sup>23,24</sup> In 1938, the first commercial alkylation plant, which used sulfuric acid as a catalyst, was built in Texas by the Humble Oil Company. The technology featuring sulfuric acid was dominant until the mid-1970s (75%) when HF catalysis became more important until an alkylate yield similar to that was obtained with H<sub>2</sub>SO<sub>4</sub>.<sup>25</sup> Initially, alkylate production was focused on meeting the demand for high-octane fuels for allied aviation during World War II; the catalysts in the alkylation plants were H<sub>2</sub>SO<sub>4</sub> and HF.<sup>26,27</sup> Starting in 1950, the production of alkylate gasoline for automobile engines began; however, its use still needed to be improved because this component of the gasoline pool was expensive.<sup>28</sup> With the continuous enactment of stricter legislation for environmental care, the alkylate component of the gasoline pool has become highly relevant, and currently, premium gasoline can reach up to 60% of the content.<sup>27</sup> Nowadays, most

industrial processes use sulfuric acid as a catalyst because it is more economical, safer to handle, and more environmentally friendly than HF.<sup>29</sup>

Almost all alkylates are obtained by using sulfuric acid or HF. The license holders that are used to produce alkylates employing H<sub>2</sub>SO<sub>4</sub> are ExxonMobil (auto cooling process) and DuPont STRATCO (Stratford Engineering Corporation) (flow cooling process). Currently, the only one with the license to obtain alkylate by means of HF is UOP LLC.<sup>27</sup> There are other technologies with which alkylate is produced, such as Honeywell UOP, which commercialized the ISOALKY process in 2016, an alkylation technology developed by Chevron USA, and the Ionikylation technology developed by PetroChina, which installed its first commercial unit in 2013. Both technologies use ionic liquids (ILs) in the production of alkylates. In 2015, the first unit using a solid acid catalyst was installed with Albemarle AlkyStar technology, and the catalyst was based on zeolites.

Therefore, this chapter will review the commercial alkylation processes using H<sub>2</sub>SO<sub>4</sub> and HF acidic liquid catalysts and the current developments using IL catalysts and solid catalysts such as zeolites.

## 5.2 ALKYLATION USING STRONG ACIDS

### 5.2.1 SULFURIC ACID

Concentrated sulfuric acid is used as a liquid catalyst to produce alkylate gasoline by reacting isobutane with olefins such as propylene, butylenes, or amylens (C3–C5 olefins). Butylenes are the primary raw materials for obtaining the highest quality alkylates. The result is highly branched (C7–C9) hydrocarbons, mainly iso-octanes, which have the highest RON (90–98) and MON (88–95) number values. In practice, alkylate is a complex mixture of isoparaffins and other hydrocarbons.<sup>30</sup> Until 1996, the most widely used acid catalyst was HF. Due to its high toxicity (when leaked, it can cause dangerous and stable aerosols<sup>31,32</sup>), more emphasis has been placed on the development of sulfuric acid-based technology and, in many industrialized countries, licenses for the construction of new HF-based alkylation plants are no longer available.<sup>33</sup> Alkylate is a premium component of the gasoline pool because it has outstanding antiknock properties and can combust cleanly.<sup>34</sup> As expected, using a catalyst in the olefin reactions (C3–C5) and isobutane allowed milder reaction conditions, temperatures below 50°C and pressures below 30 bars. The alkylate quality depends on factors such as the initial olefin mixture, isobutane-to-olefin ratio, H<sub>2</sub>SO<sub>4</sub>-to-reactants ratio, and stirring efficiency.<sup>35,36</sup>

The olefins fed to the alkylation unit generally come from an FCC unit and the main components are butene and isobutene and minor amounts of propane and amylens. Water is removed from this stream. Isobutane comes from the catalytic reforming unit stream (70% vol.) and the high purity (over 95% vol.) comes from the alkylation unit of the deisobutanizer tower.

In the STRATCO effluent-cooled process (Figure 5.2), olefins, isobutane, and recycled acid are introduced into the reactor (a continuous flow stirred tank) and emulsified using a high-power mixer located at one end of the reactor for 20–35 min. The hydrocarbon mixture with the acid is circulated through the heat transfer tubes

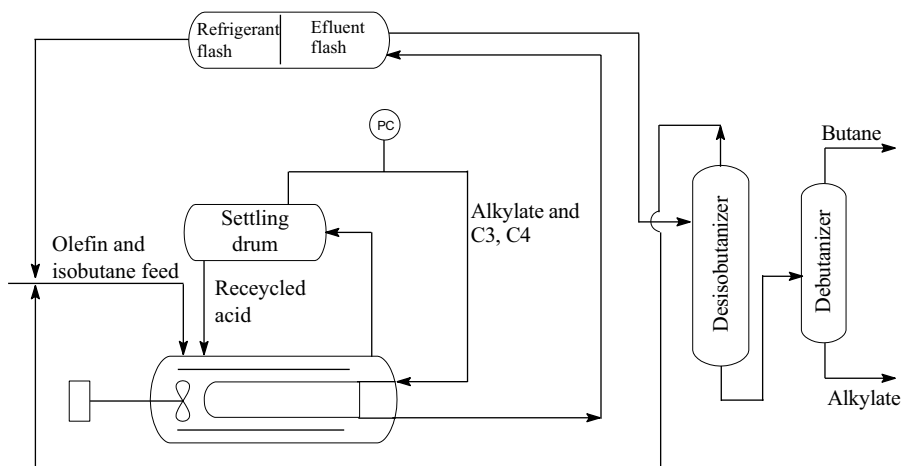


FIGURE 5.2 Alkylation unit of the refrigerated STRATCO effluent process.

repeatedly. Once the reaction is complete, the emulsion passes into a decanter, where the acid is separated by gravity from the hydrocarbons for 30–60 min. The separated hydrocarbon stream may contain approximately 80 wt. % of isobutane. This stream is reduced in pressure so that the light hydrocarbons evaporate (flash) and the temperature of the liquid hydrocarbons decreases, which is used as the cooling stream in the reactor. Most of the acid is recycled to the reactor and the portion of acid that is not recycled is replaced by fresh acid (98%). The acid concentration was kept above 90% for optimum selectivity and activity. The temperature in the reactor depends on the composition of the olefin feed; when the feed stream has butenes and pentenes, it is between 1 and 5°C and when it is a propylene-rich stream, it is 10°C.

In ExxonMobil's self-cooling cascade alkylation process (Figure 5.3), olefins, acid, and isobutane, which also act as a coolant, are introduced into the first zone of the cascade reactor. In the next reactor zones, isobutane/olefin mixtures are injected

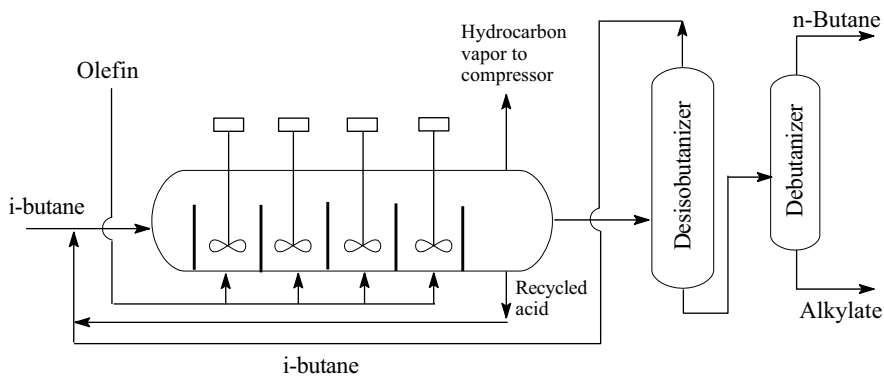


FIGURE 5.3 Alkylation unit of the autorefrigeration ExxonMobil process.

at ratios ranging from 8:1 to 12:1. Each zone of the cascade reaction enters an emulsion of acid and hydrocarbons from the previous zone. Starting from the second reaction section, the hydrocarbon in the emulsion is mainly composed of isobutane and alkylate. In the first reaction zone, the lowest temperature (1.2°C) and higher concentration of isobutane are recorded and the best alkylate is obtained. As one moves to the next reaction zone, the temperature increases (up to 7°C), and because the concentration of olefins introduced into each reaction zone increases, the quality of the alkylate decreases.<sup>37</sup> The evaporating gases are compressed and sent to the feed, which allows the cooling of the feed stream. After the last reaction zone is allowed to settle, the acid phase is pumped to the feed and the hydrocarbon phase in the treatment zone of these effluents (mainly isobutane) is recovered in the deisobutanizer to recycle it again.

In hydrocarbon streams, sulfate esters are obtained, which are removed by caustic washing. An alternative is acid washing, which unlike caustic washing, can produce more alkylate, regenerate the acid, and consume less acid.<sup>38</sup>

STRATCO reactors are designed to produce around 2,500 barrels of alkylate per day compared to ExxonMobil reactors, which are designed to produce between 3,000 and 10,000 barrels per day. The former allows greater operating flexibility. The significant cost associated with the alkylation process is due to the high sulfuric acid consumption (70–100 kg of acid per metric ton of alkylate) and the high energy consumption required to recover the deactivated acid (2–3 times more expensive than fresh acid).<sup>39,40</sup>

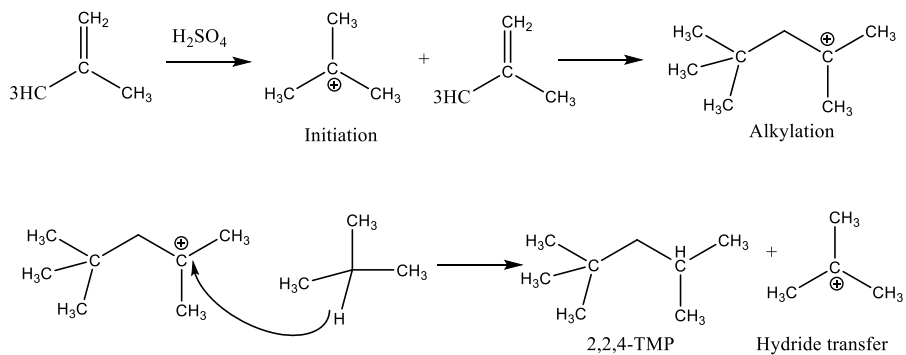
In industrial alkylation reactions, a large number of isoparaffins can be detected, between 130–150 (C5–C16);<sup>41</sup> many of the reaction products are isomers, so there is a complex distribution, and it is far beyond obtaining trimethylpentane (TMP) isomers (RON 100–109.6), which are the most desired products.<sup>42</sup> Other products such as C5–C7 (light ends) (RON 24.8–93), dimethylhexanes (DMH) (RON 55.5–73.6), methylheptanes (RON 21.7–26.8), and C9+ (heavy ends) (RON 70–91) are also obtained.<sup>43</sup>

The carbanion chain reaction mechanism mainly drives the reaction between *i*-butane and light olefins, which is catalyzed by concentrated sulfuric acid.<sup>43,44</sup> Olefins are converted to butyl carbocations by protonation of the double bonds to yield *sec*-butyl or *tert*-butyl cations<sup>45,46</sup> that can be dimerized or oligomerized with olefins to generate larger C8 to C12 carbocations. These larger carbocations can undergo cracking, resulting in light carbocations (C5–C7).<sup>47,48</sup> To complete the chain reactions, the hydride transferred between the TMP carbocation and isobutane forms TMP and an *i*-butyl cation (Figure 5.4).<sup>49</sup>

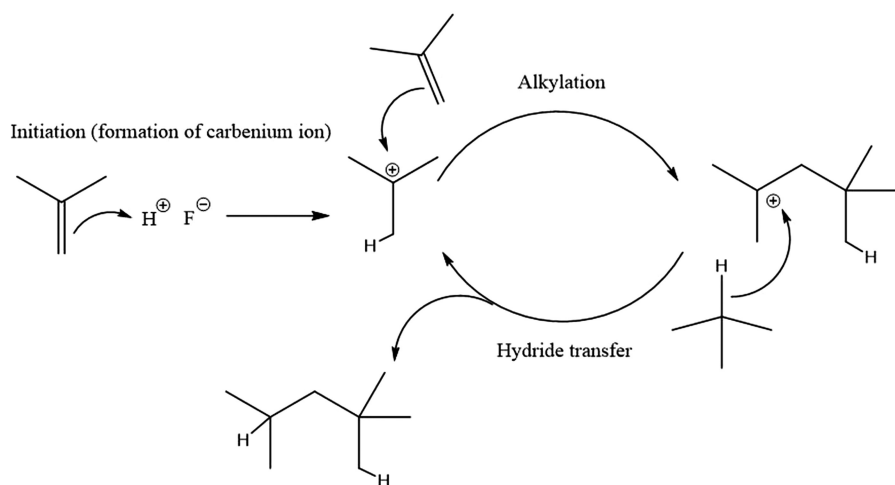
### 5.2.2 HYDROFLUORIC ACID

As well as sulfuric acid, the alkylation reactions using HF are important in organic chemistry for introducing an alkyl group to a substrate. Also, HF is another strongest Lewis acid that can activate electrophiles and nucleophiles, making it a versatile reagent for alkylation reactions. Table 5.1 describes the properties of HF, where the Hammett acidity value is lower than that of sulfuric acid.<sup>26,50</sup> However, it is important to note that HF is a very toxic and corrosive acid that can attack and corrode glass surfaces.

The alkylation reaction process for obtaining gasoline in petroleum refining is similar to that of using sulfuric acid<sup>50</sup>. Additionally, it produces high-octane gasoline



**FIGURE 5.4** Simplified general scheme of the reaction mechanism between isobutylene and isobutane.



**FIGURE 5.5** Alkylation mechanism with HF as catalyst.

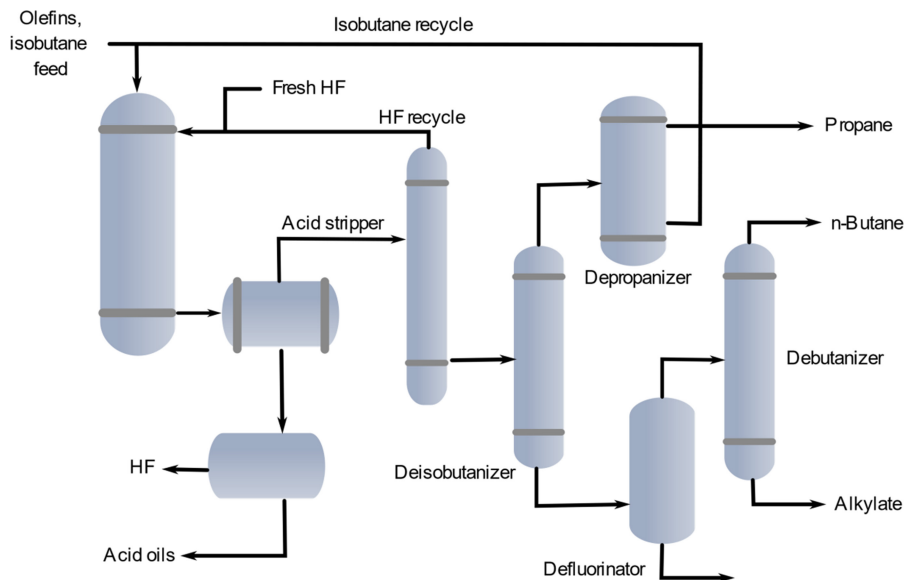
components. It combines light and gaseous hydrocarbons (C3 to C5) to form heavier (C6 to C12)-branched chain hydrocarbons with excellent antiknock properties.

The mechanism of the alkylation reaction in HF is very well known and consists of the conversion of butenes and *i*-butenes to produce alkylate derivatives in three steps: the first one is the protonation of alkene derivatives to form carbenium ions, the second one is the alkylation reaction, and finally, hydride migration occurs to obtain the alkylate product, and the new carbenium species continue the catalytic cycle (Figure 5.5).<sup>50</sup>

As discussed below, strong acids are the best catalysts for alkylation reactions. However, the use of HF (although it is a better catalyst and industrially used) is associated with problems and serious challenges in terms of environmental aspects, corrosion problems in plants, and intrinsic handling danger.

In the refinery, when HF is used as a catalyst, the unit is called a HF alkylation unit (HFAU) and requires expensive corrosion-resistant materials for building the equipment. In general, the description of the HFAU is as follows: the first step of the reactor





**FIGURE 5.6** Schematization of the HFAU to obtain alkylate.

consists of olefin and isobutane feed treatment for coalescence and removal of water, sulfur, and other contaminants; later, the mixture of olefins and isobutene is passed to the reactor (with reaction chambers filled with HF); after the alkylation reaction occurs, the reactor effluent goes to a settler to separate the C7–C8 naphtha range product from the acid (this acid is separated and recirculated to the reactor); the alkylate fraction is washed in a caustic scrubber and later sent to a fractionation unit; in this last step, the fractionation consists of the deisobutanizer and depropanizer processes for obtaining the alkylate that is sent to gasoline pool blending. Figure 5.6 schematizes the whole described process. The operation conditions in the presence of sulfuric acid are discussed below and are similar to those in the presence of HF.<sup>51,52</sup>

It is important to highlight that the HFAU is provided mainly by UOP Honeywell at the industrial level.

The next sections will discuss the main alternatives to replace HF as a catalyst in industrial processes to maintain optimal yields in the alkylate reaction and avoid the challenges of its use in alkylation units.

### 5.3 OTHER CATALYSTS USED IN THE ALKYLATION REACTION

The following sections describe the problems, challenges, safety considerations, disposal of wastes, and expensive devices available for handling corrosive acids such as  $H_2SO_4$  and HF. Additionally, other inconveniences of using HF include its high volatility and rapid dispersion over several kilometers and the high operation cost due to the use of corrosion-resistant materials, which have resulted in the identification of new alternatives for the use of other catalysts capable of maintaining the quality of alkylates in industrial processes.<sup>50</sup>

This section discusses recent advances in finding technological solutions to replace  $\text{H}_2\text{SO}_4$  and HF with promising alkylation catalysts that improve the reactivity and selectivity of alkylation products for gasoline blending. These new materials are catalysts based on Brönsted acids (acidic chloroaluminates), ionic liquids (ILs), zeolites, or their combinations.

### 5.3.1 IONIC LIQUIDS (ILs)

From the challenge discussed above in using  $\text{H}_2\text{SO}_4$  and HF as catalysts, ILs have emerged as alternatives or promoters of alkylation reactions. ILs have unique and interesting physicochemical properties such as being liquid salts at room temperature, acting as polar solvents and ionic salts, nonvolatility, thermal stability, ionic conductivity, and recyclability, and these properties are modulable to enhance or obtain a great variety of these compounds. In this way, ILs have been found in various applications, such as hydrogenation, oxidation, extraction, and isomerization. Moreover, catalytic applications for obtaining high-quality gasoline alkylates have been explored.<sup>53</sup>

If an IL is used, it needs a series of characteristics to be considered a good catalyst in an alkylation reaction: high acidity, such as a Lewis or Brönsted acid. These properties could be modulated through the design of the anionic or cationic fragments; in this sense, a recent review has provided a complete discussion about the use of ILs in alkylation reactions.<sup>54</sup> The mechanism of the alkylation reaction is similar to that using mineral acids, with differences in the type of acidity provided by the IL.

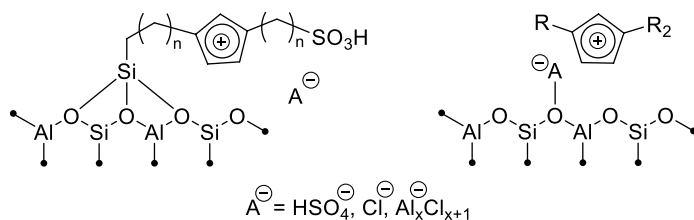
For example, Brönsted acidic ILs are based on  $[\text{N-H}]^+$ -type protic cations that work as proton donors and the anion stabilizes the species during the catalytic cycle. On the other hand, other ILs are based on sulfonic groups in the anion fragment and act as proton donors. In contrast, ILs based on Lewis acids are also used. The main reason is that Brönsted acidity is insufficient to achieve the best conversion or selectivity. For Lewis acid-based ILs, the presence of strong Lewis acids such as  $\text{Al}_2\text{O}_7^-$ ,  $\text{Zn}_2\text{Cl}_5^-$ ,  $\text{CuAlCl}_5^-$  etc. in the anion fragment increases the acidity of the IL. Combinations of Brönsted–Lewis acids in the structure of ILs also exist to establish a synergistic effect to increase the acidity of the whole compound. There are other combinations where the acidic IL is mixed with mineral acids, such as HCl or mixed with inorganic salts, such as Lewis acids, for example, CuCl,  $\text{AlCl}_3$ ,  $\text{FeCl}_3$ ,  $\text{ZnCl}_5$ ,  $\text{CuCl}_2$ , AgCl,  $\text{ZnCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{CeCl}_3$ ,  $\text{SnCl}_2$ , ZnO, and CuO.<sup>54</sup>

The general structures of ions featured in ILs with Brönsted acidity, Lewis acidity, and their synergistic combinations used as catalysts in alkylation reactions are shown below in Figure 5.7.

The mechanism of the alkylation reaction using an IL is similar to that of the conventional catalytic cycle with mineral acids (Figure 5.8): once the IL reacts with the olefin to form the carbenium species, it reacts with another alkene to undergo the alkylation process, followed by an isomerization step, and finally, hydride transfer to produce the alkylate product, recovering another carbenium ion to continue the catalytic cycle.<sup>39</sup>

Additionally, organic or inorganic additives are sometimes added to increase the catalytic activity of ILs. For example, if CuCl,  $\text{CuCl}_2$ , or  $\text{NiCl}_2$  is incorporated into





**FIGURE 5.9** Schematic structure of ILs immobilized on a zeolite surface.

Of course, the employed ILs need to have the characteristics of Brönsted or Lewis acid groups, which in turn, contribute to the acidity of the support and increase both the alkylate yield and selectivity to TMP. Some examples of used ILs are based on imidazolium cations, such as 1-butyl-3 triethoxysilylpropyl-imidazolium hydrogen sulfate.<sup>54</sup> However, these new catalysts are currently under investigation. Figure 5.9 shows a general scheme of the support and IL immobilization.

It is important to highlight that ILs can be prepared at the industrial level;<sup>55</sup> this fact represents an opportunity to implement them in industrial processes.<sup>56</sup> In this sense, there are two examples of the use of ILs in alkylation plant refineries. The first one is the Isoalky™ technology<sup>57</sup> developed by Chevron and Honeywell UOP and installed in Salt Lake City. This refinery is the first in the world to implement an alkylation unit based on an IL capable of producing 5000 barrels/day of alkylate.<sup>58</sup> This process represents a major innovation in alkylation technology. The second one is the Ionikilatyon™ technology<sup>59</sup> developed by the China University of Petroleum and licensed by Well Resources from Canada; now, six units in China have been installed to produce 7500 barrels/day of alkylate. These two industrial technologies are described below.

### 5.3.1.1 Isoalky™ Technology

The catalyst in the Isoalky™ process is a chloroaluminate-based IL, where the cation is an ammonium or phosphonium ion and the anion is  $AlCl_4^-$  or  $Al_2Cl_7^-$ . This catalyst exhibits high activity and selectivity to alkylation and long thermal stability. Additionally, a trace amount of HCl is needed as a cocatalyst, which is generated *in situ* through the addition of an organic chloride promoter.<sup>60</sup> This technology exhibits a series of benefits:

- The refinery produces an equal or greater volume of alkylate with less catalyst amount and a smaller reactor (3–6% of catalyst).
- The reaction produces higher octane gasoline or maintains the conventional gasoline pool.
- The Isoalky™ unit provides the refinery with the option to use whichever feedstock.
- Isoalky™ technology could upgrade C3–C5 with maximum feed efficiency.
- There is a low degree of polymerization of olefins. In other words, the alkylate yield is higher. On the other hand, polymers are converted into regenerated naphtha and blended back into alkylate gasoline, providing additional yield.

- Reduced environmental impact due to the fact that online regeneration eliminates polymer or catalyst incineration. A smaller reactor generates a smaller volume or reduces the amount of acidic and caustic products.

### 5.3.1.2 Ionikilasyon™ Technology

PetroChina Dagang Petrochemical Co. has commissioned a new unit based on IL alkylation technology to produce high-octane alkylate in its 5 million/year refinery.

The Ionikilasyon™ technology is based on nontoxic ILs with a fraction of  $\text{AlCl}_3$ ,  $\text{HCl}$ , and  $\text{CuCl}_2$ . This IL-based composite is the catalyst and has adequate handling behavior. The process consists of several stages: the first one is feed pretreatment and the second one is the alkylation reaction, followed by the separation of products and catalyst regeneration.<sup>61–63</sup> Ionikilasyon™ offers the following advantages over conventional alternatives:

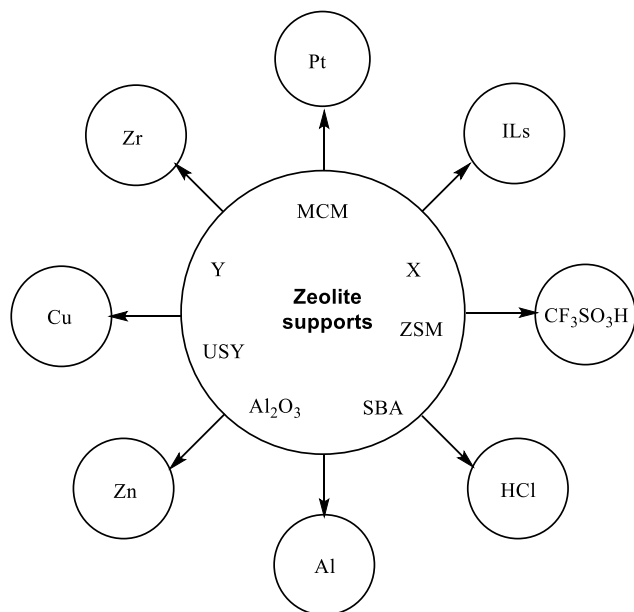
- Innovative technology with multiple commercial units.
- The use of corrosive  $\text{HF}$  and  $\text{H}_2\text{SO}_4$  catalysts was eliminated.
- Safer process, noncorrosive system, and low-cost carbon steel equipment.
- Nonhazardous emissions of waste and reduced energy consumption: environmentally friendly.
- High catalyst activity and stable reactor operation conditions.
- High-quality alkylate products (96–98 RON).
- Integrated catalyst regeneration.

This fact can be seen after the analysis of two main industrial technologies. The beneficial aspects are excellent, and they are significant in the safer operation, adaptability of the technologies over the existing refineries, and, of course, the successful commercial test.

### 5.3.2 ZEOLITES

It is well known that heterogeneous catalysts are widely used in crude oil refining catalytic processes, such as FCC, Fisher–Tropsch, hydrotreatment processes, etc. The following section discusses the use of Brønsted and Lewis acids such as  $\text{AlCl}_3$ ,  $\text{SbF}_5$ , or  $\text{BF}_3$ -based catalysts. However, other inorganic solids that exhibit acidic properties, such as zeolites, zirconia, a mixture of oxides, or acidic resin, have been studied by many researchers for alkylation reactions.<sup>26,50</sup>

In this sense, zeolites have a large surface area due to their large porosity, exhibit acidic properties, have exceptional thermal stability, and have the ability to undergo hydride transfer. However, rapid deactivation due to coking represents an operational disadvantage because zeolites depend on additional regeneration processes. Although this operation is well known in the oil industry, it does not represent a serious challenge. Among the zeolites that are more commonly employed in alkylation reactions are Y-zeolites, X-zeolites, MCM-22, USY, ZSM, and SBA; some of these incorporate promoters or cocatalyst substances to enhance or improve the acidic properties, such as Pt, Zr, Ce, Cu, Zn, Al, or  $\text{HCl}$  or  $\text{CF}_3\text{SO}_3\text{H}$  acids, and as it was mentioned above, functionalized ILs (Figure 5.10).<sup>50,54,64</sup>



**FIGURE 5.10** Main zeolite supports and promoters used in the alkylation process.

Of course, zeolite-based catalysts for the alkylation process have been developed commercially. Here are some examples:

### 5.3.2.1 AlkyClean™ Process

This technology was developed by CB&I, Albemarle Corp., and Neste Corp. It was the first commercial-scale process based on a solid acid catalyst. The unit for alkylation has a capacity of 2700 barrels/day for alkylate production. The technology employs Pt/US-Y, a fixed zeolite developed by Albemarle with the trade name AlkyStar. The general process uses a series of reactors with distributed injection olefin feeds to achieve high isobutane/alkene ratios. This process requires an additional regeneration step at 250°C in a hydrogen atmosphere.<sup>50</sup>

### 5.3.2.2 K-SAAT™ Technology

The next-generation solid acid alkylation technology was developed by M/s KBR and Exelus. The catalyst is a zeolite Y-based ExSact and a precious metal-free material, which provides superior alkylation performance with an alkylate with RON >99%. This K-SAAT process is more efficient, cost-effective, and environmentally benign than liquid mineral acids. KBR has signed two K-SAAT licenses: the first one to Dongying Haike Ruilin Chemical Co. Ltd., in Shandong Province, China, and the second one to Luoyang Aiyou Chemical Co., in Henan Province, China.<sup>65</sup>

### 5.3.2.3 Lurgi EuroFuel® and Haldor Topsoe FBA™ Processes

Lurgi and Süid-Chemie AG developed another zeolite-based technology for the alkylation process known as EuroFuel®, consisting of a Y-zeolite with a high

**TABLE 5.2****Comparison of the Different Technologies Used for the Alkylation Process in the Industry**

Catalyst	T (°C)	P (psi)	Isobutane/ Olefin Ratio	RON	Catalyst %	Corrosion Level
H <sub>2</sub> SO <sub>4</sub>	0–15	30–80	7–15	95–96	50	High
HF	35	200	10	95	60–75	High
Isoalky™	0–50	40–250	8	94–99	3–6	Low
Ionikylation™	10–25	110–170	8–10	96–98	ND	Low
AlkyClean™	50–90	1–100	8–10	91–94	20–80	Low
EuroFuel®	50–100	ND	6–12	ND	ND	Low
K-SAAT™	60–71	ND	8–15	>99	ND	Low

ND: not available

concentration of Brønsted acid sites and lower Lewis acid sites. The reactor is based on a distillation tower concept, where the catalyst is mixed with the isobutane feed and the alkene at the top isobutane mixture is introduced at stages: the catalyst is mixed as a consequence of boiling the mixture of alkylate and isobutane. Haldor Topsoe has developed a fixed-based alkylation (FBA™) process that employs a liquid catalyst: trifluoromethanesulfonic acid supported on a zeolite.<sup>66</sup> Information about these processes is scarce due to them being maintained as an industrial secret.

Table 5.2 shows the main characteristics of the alkylation processes using mineral acids (conventional catalysts), IL technologies, and zeolite-based technologies implemented at the industrial level in the alkylation process to obtain gasoline.

## 5.4 CONCLUSIONS

This chapter analyzed and compared conventional alkylation processes, which use H<sub>2</sub>SO<sub>4</sub> and HF, and are now firmly established industrial processes for obtaining almost all alkylation gasoline globally. New technologies based on solid catalysts, such as the AlkyClean process, K-SAAT technology, Lurgi EuroFuel, and Haldor Topsoe FBA processes, and ILs, such as the Isoalky technology and the Ionikylation technology, were also discussed. Technologies using ILs as catalysts have proven to be a viable alternative to those using strong acids such as H<sub>2</sub>SO<sub>4</sub> and HF because they have high conversion and selectivity, the catalysts can be regenerated, and they are considered more environmentally friendly.

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