

Review of Petroleum Refinery Acid Catalyzed Alkylation Processes: A Message to Nigerian Refineries

By

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Abstract

The existing Alkylation Plants in the country are HF catalyzed, and have been abandoned many years ago due to the dangers of the catalyst contact with man on exposure to it. In other parts of the world, Alkylation capacity is growing more rapidly worldwide while there is incremental capacity addition in the USA as refiners reduce TEL levels and increase conversion capacity and their ability to produce larger volumes of cleaner burning gasoline primarily in response to reformulated gasoline (RFG) requirements and the impending phase out of methyl-tert-butyl ether (MTBE). Several refiners have developed and expressed interest in adoption of STRATCO's ALKYSAFE Process. This low capital HF to H₂SO₄ Conversion/Expansion has a clear potential of improving the alkylate quantity and quality from existing HF alkylation units. Currently in order to minimize the dangers of existing HF alkylation units, HF modifiers that reduce the aerosol potential of HF are being used along with mitigation systems. Research continues on a solid catalyst for alkylation, but no technology has been commercialized yet. Due to heightened concerns over the safety of HF, the majority of alkylation units installed in the last ten years use H₂SO₄ catalyst. It is recommended strongly that new proposed refineries must be H₂SO₄ Alkylation catalyst compliant for a safer operation and working environment as continuing refinery processing changes is certain with a focus on both improved product quality (octane) and quantity for cleaner burning fuels well into the decades ahead.

Background

Petroleum Refinery can technically be defined as a technological establishment primarily engaged in manufacturing and producing light petroleum products such as gasoline (petrol), kerosene, distillate fuel oils, residual fuel oils, and lubricants through straight distillation of crude oil, redistillation of unfinished petroleum products derivatives, cracking and other processes, according to the needs of the location it will serve. It also produces light gases, aliphatic and aromatic chemicals as by-products which serve as feedstock for the petrochemical industry. Nigeria, has four aged refineries namely: Port Harcourt Refining Company Limited (PHRC); Warri Refinery and Petrochemicals Company Limited (WRPC); Kaduna Refinery and Petrochemicals Company Limited (KRPC). The PHRC system comprises the old refinery which is simple and a new one which was then more sophisticated and modern. The refinery was expected to provide qualitative and quantitative refining services for the domestic and international markets at competitive prices.

The major products of PHRC system include transportation fuels (gasoline and diesel) otherwise known as Premium Motor Spirit (PMS) and Automobile Gas Oil (AGO). Liquefied petroleum gas, LPG, and kerosene, which are also used as jet fuel and fuel oil (mazout) are also produced from the atmospheric distillation unit. It is important to note that valuable low sulphur atmospheric residue was exported to European countries for their fuel oil needs in power generation. Nigeria then utilized hydroelectric power and coal for energy needs.

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In 1974, crude oil sales revenue was used in building two grassroots refineries WRPC commissioned in 1978 and KRPC in 1979. WRPC had an installed capacity of 100,000BPSD. These were more complex refineries than the first PHRC. These latter refineries' configuration incorporated chemical conversion units viz; fluid catalytic cracking unit and catalytic reforming plants as well as HF alkylation units³ (See Table 1) in order to meet the increasing demand for high octane motor fuels.

Table 1 Process Units of Nigerian Refineries and Alkylation

| Refinery Units | PHRC Capacity (bpd) | WRPC Capacity (bpd) | KRPC Capacity (bpd) |
|------------------------------|----------------------------|----------------------------|----------------------------|
| Crude Unit | 210,000 | 125,000 | 110,000 |
| Vacuum Unit | 54,000 | 34,200 | 38,200 |
| Catalytic Reformer | 39,000 | 21,000 | 17,500 |
| FCCU | 40,000 | - | 21,000 |
| Kerosene Hydrotreater | 33,000 | 15,800 | 17,500 |
| Naphtha Hydrotreater | - | - | 24,000 |
| LPG unit | - | 6,000 | - |
| Alkylation Unit | 7,020 | 2,850 | - |
| Isomerisation Unit | 3,600 | - | - |

The pathetic state of the Nigerian Petroleum refining industry today cannot be overemphasized. Many efforts by different governments have been made in the past to improve the production capacity of these refineries to help in alleviating the pains of the population in fuel demand. Recently, Nigerian officials announced a \$4.5 billion deal that will see the country partner with US Company Vulcan Petroleum Resources to build six more oil refineries in the country. In January, 2012, there were mass protests throughout the Country when the government initiated a removal of fuel subsidy, which was the only perceived benefit many Nigerians enjoyed from the nation's oil wealth. The government later announced a partial subsidy as the country could no longer afford the \$8 billion fuel subsidy⁴. The refineries do not meet the refined products needs of Nigeria. Nigeria will no doubt continue to import turnkey plants because of the level of local technology, but decisions on issues of protection of life and environment should not be left in the hands of politicians alone but academic researchers and professionals should be engaged in consultations regarding global best practice in the purchase of technology or technology transfer.

Current Trends in Acid Catalyzed Alkylation Processes

A study of the operational performance of the installed alkylation units has been done and current trends of utilization of acid catalyzed alkylation reactions in the world had been carefully studied in the face of stringent economic and environmental regulations. Refiners, worldwide, are producing cleaner burning or reformulated gasoline (RFG) to meet requirements of environmentally driven legislation. Other countries generally follow U.S.

³ Akpabio, E.J (2006): Challenges of the Contemporary Petroleum Refining Industry in Nigeria. Proceeding of the Nigerian Society of Chemical Engineers Conference, Ibadan.

⁴ Albright, L.F (1977) : Industrial and Laboratory Alkylation, ACS Symposium Series No 55, Pp 128-146, American Chemical Society, Washington, D.C.

environmental policy and will hopefully learn from their experience and mistakes. The World Bank has called for a worldwide ban on leaded gasoline and most population centers of the world are moving toward reformulated gasoline to reduce air pollution. Regulations that will mandate gasoline reformulation to reduce motor vehicle emissions during the 1990s will boost the importance of the alkylation process in U.S. refineries. Highlighting the role of alkylates⁵, affirms that constituents in the alkylate produced do not contribute to ozone formation. The low vapor pressure of alkylate, a high octane blending component, helps refiners maintain volatility (Rvp) specifications. Alkylation offers several key advantages to refiners, including the highest average quality of all components available to the gasoline pool, increased amounts of gasoline per volume of crude oil, and high heats of combustion. Alkylates permit use of internal combustion engines with higher compression ratios and hence the potential for increased distance per litre. Alkylates burn freely, promote long engine life, and have low levels of undesired emissions. Prakash⁶ asserts that Alkylation is important refining processes for the production of alkylate a high-octane and excellent gasoline blending component. Alkylate product is a mixture of branched hydrocarbons of gasoline boiling range. Alkylate has a motor octane (MON) of 90-95 and a research octane (RON) of 93-98.

While gasoline is in oversupply in Europe and demand is flat, alkylation continues to be of importance as the countries move toward a higher percentage of unleaded gasoline as well as requirements for lower benzene and aromatics levels. Russia and the countries making up the former Soviet Union do not have reformulated gasoline regulations in place but recognize an increasing demand for alkylate as they reconfigure and modernize their refineries with a view to export gasoline to Europe. Many gasoline-producing complexes are being studied and re-engineered; these complexes shall include FCC, MTBE and alkylation units.

The term alkylation refers to any reaction that adds an alkyl group to a molecule. To the refiner, it means the reaction of a low molecular weight olefin (*e.g.*, propylene, isobutylene) with an isoparaffin (*e.g.*, isobutane) to form heavier isoparaffins with high octane values. Alkylation is unique compared to the other catalytic processes in that alkylation uses a liquid acid catalyst instead of a solid catalyst (although there are ongoing projects to develop a solid acid catalyst for alkylation). Even though catalysts are not consumed in the chemical reactions they promote, they can be deactivated and diluted by contaminants present in the feed streams to the catalytic processes, and eventually all catalysts must be replaced.

Either sulphuric acid (H₂SO₄) or hydrofluoric acid (HF) catalyst is used in the process. The process yields a wide range of products, and conditions are controlled to maximize octane values rather than to yield specific chemical compounds⁷. Alkylation in petroleum processing produces larger hydrocarbon molecules in the gasoline range from smaller molecules⁸. The products are branched hydrocarbons having high octane ratings. Alkylates are the best of all possible motor fuels, having both excellent stability and a high octane number⁹. Olefins of 3 to 5 carbon atoms (*e.g.*, from catalytic cracking and coking) react with isobutane (*e.g.*, from catalytic cracking) to give high octane products. Sulfuric (H₂SO₄) or hydrofluoric (HF) acid

⁵ Albright, Lyle F. (1990): Modern Alkylation will be key process in Reformulated Gasoline Era. Oil and Gas Journal November 12, Vol.88(46).

⁶ Prakash S. (2003): Refining Processes handbook, Elsevier Books Ltd. Pp 125-300.

⁷ Albright, L.F, Spalding, M.A, Faunce,J and Eckert,R.E (1988): Industrial Engineering Chemistry Research, Vol. 27(391).

⁸ Cheung, T and Gates,B (1997): Strong Acid Catalyst for paraffin Conversion, CHEMTECH Vol. 27(9), Pp28-34.

⁹ D'Aquino, R and Mavridis,L (2007): Solid acid Catalysts Shape up for Alkylation. Chemical Engineering Progress, Vol.103 (1), Pp 8-9.

act as catalysts. Spent sulfuric acid, sulphuric acid alkylation sludges, and HF sludges are listing residuals, while spent HF acid, acid soluble oil and treating clays are residuals¹⁰.

These acid catalysts are capable of providing a proton, which reacts with the olefin to form a carbo-cation. Although this reaction is simply the reverse of cracking, the belief that paraffin hydrocarbons are chemically inert delayed its discovery until about 1935¹¹. The need for high-octane aviation fuels during World War II stimulated the development of the alkylation process for production of isoparaffinic gasolines of high octane number. Although alkylation can take place at high temperatures and pressures without catalysts, the only processes of commercial importance involve low temperature alkylation conducted in the presence of either sulfuric or hydrofluoric acid. By proper choice of operating conditions, the alkylate can be made to fall within the gasoline boiling range with motor octane numbers from 88 to 94 and research octane numbers from 94 to 99¹². Alkylate is in short supply in the Nigeria. The renewable fuels standard (RFS) mandates the use of ethanol in gasoline. The high vapor pressure of ethanol requires a reduction in other light gasoline components such as butanes and pentanes in order to meet federal Reid vapor pressure standards. The butane and pentane loss will be about 0.4 gal/1 gal of ethanol added to the gasoline pool.

Octane-based alkylate is thus a key alternative to compensating for the loss of these light components without adding to the aromatic or olefinic content of the gasoline. A severe alkylate shortage contributed to a spike in gasoline prices in summer 2008 in America. Making matters worse, several hydrogen fluoride alkylation units have been shut down over the last decade. HF alkylation units require extremely high levels of maintenance to ensure safe operation. Accidents have, in some cases, convinced the refinery management to moth ball these units. Three separate accidents involving HF releases at US refineries occurred in a 5-month span during 2009, leading to prolonged shutdowns and investigations by the US Chemical Safety and Hazard Investigation Board, Washington.

Process Variables of Acid Catalyzed Alkylation Processes

In alkylation processes using hydrofluoric or sulfuric acids as catalysts, only isoparaffins with tertiary carbon atoms, such as isobutane or isopentane, react with the olefins. In practice only isobutane is used because isopentane has a sufficiently high octane number and low vapor pressure to allow it to be effectively blended directly into finished gasoline. The process using sulfuric acid as a catalyst is much more sensitive to temperature than the hydrofluoric acid process. With sulfuric acid it is necessary to carry out the reactions at 5 to 21°C or lower, to minimize oxidation reduction reactions which result in the formation of tars and the evolution of sulphur dioxide. When anhydrous hydrofluoric acid is the catalyst, the temperature is usually limited to 38°C or below. In both processes, the volume of acid employed is about equal to that of the liquid hydrocarbon charge and sufficient pressure is maintained on the system to keep the hydrocarbons and acid in the liquid state. High isoparaffin/olefin ratios (4:1 to 15:1) are used to minimize polymerization and to increase product octane. Efficient agitation to promote contact between the acid and hydrocarbon phases is essential to high product quality and yields. Contact times from 10 to 40 minutes are in general use. The yield, volatility, and octane number of the product is regulated by adjusting the temperature, acid/hydrocarbon ratio, and isoparaffin/olefin ratio. At the same operating conditions, the products from the hydrofluoric and sulfuric acid alkylation process

¹⁰ Dittrick, P (2009): USW seeks Phase out of HF Alkylation Units OJG On-Line, Aug 31, 2009.

¹¹ Erikh, V.N, Rasina M.G and Rudin, M.G(1988): The Chemistry and technology of Petroleum and Gas. Mir Publishers, Moscow, Pp 283-292.

¹² Gary, James H and Handwerk, Glenn E (2001) : Petroleum Refining Technology and Economics, Fourth Edition. Marcel Dekker Inc, Pp 84-89.

are quite similar. For both processes the more important variables are the Reaction temperature, acid strength, isobutane concentration, and olefin space velocity.

Vigorous mixing of hydrocarbon and acid is very beneficial for the reaction. Increased mixing produces a finer dispersion of hydrocarbon droplets in the acid continuous phase emulsion, increasing the surface area for mass transfer of isobutane into the acid catalyst. This improves the product quality and reduces acid consumption.

Reaction temperature

With sulfuric acid it is necessary to carry out the reactions at 5 to 21°C or lower, to minimize oxidation reduction reactions which result in the formation of tars and the evolution of sulphur dioxide. When anhydrous hydrofluoric acid is the catalyst, the temperature is usually limited to 38°C or below.

Acid strength

The acidity of hydrofluoric acid solutions varies with concentration owing to hydrogen-bond interactions of the fluoride ion. Dilute solutions are weakly acidic with an acid ionization constant $K_a = 6.6 \times 10^{-4}$ (or $pK_a = 3.18$),¹³ in contrast to corresponding solutions of the other hydrogen halides which are strong acids. Concentrated solutions of hydrogen fluoride are much more strongly acid than implied by this value, as shown by measurements of the Hammett acidity function H_0 (or “effective pH”). For 100%, HF has an H_0 , estimated to be between -10.2 and -11, which is comparable to the value -12 for sulfuric acid. The best results- the maximum yield of Alkylate, the highest octane number and minimum contamination of the products by esters, are achieved at a sulphuric acid concentration from 90 to 94%. For HF process, catalyst activity is optimal when it contains not over 1.5% of water and not over 12% of organic polymers¹⁴.

Isobutane concentration

In each case, isobutane to olefin ratio for both HF and H₂SO₄ catalyzed processes are in the same range of 3 to 12 as shown in Table 3.

Olefin Space Velocity

Because alkylation occurs almost instantaneously, the residence time of reactants is not a limiting parameter. The space velocity (*SV*) in this case may be defined as follows:

$$SV = \frac{\text{olefin in contactor (bbl/hr)}}{\text{acid in contactor (bbl)}}$$

The term is a measure of the concentration of olefins in the acid phase of the reactor. As the olefin space velocity increases, octane tends to decrease and acid consumption tends to increase¹⁵.

In deciding which alkylation process is best for a particular refinery, the following factors for the production of the desired product must be considered. Many factors are important, including total operating expenses; initial capital costs; alkylate quality; flexibility of operation; reactants available; yields and conversion of reactants; maintenance problems; safety; experience with a given process; and patents, licensing arrangements, and possible royalties.

¹³ Gruse, W.A and Stevens, D.R Chemical Technology of Petroleum, 3rd Edition.

¹⁴ Hofmann, J.E and Schriesheim, A,J (1962): American Chemical Society, Vol.84(953). McGraw-Hill Book Company, New York (1960) Pp 153-163.

¹⁵ Ikoku, C.U (2000): Petroleum; Mankind’s Best Friend. 26th Inaugural Lecture of the University of Port Harcourt, Nigeria.

Cases for Hf Catalyzed Process

Advocates of the hydrofluoric acid process argue that both capital and total operating costs are less than those of sulfuric acid processes for the following reasons:

1. Smaller and simpler reactor designs are feasible.
2. Cooling water can be used instead of refrigeration.
3. Smaller settling devices are needed for emulsions.
4. Essentially complete regeneration of the hydrofluoric acid catalyst occurs. Hence, hydrofluoric acid consumption and costs are very low. Disposal of spent acid is not necessary.
5. There is increased flexibility of operation relative to temperature, external ratio of isobutane to olefin, etc.
6. There is decreased need for turbulence or agitation when acid and hydrocarbon streams are combined.

Cases for H₂SO₄ Catalyzed Process

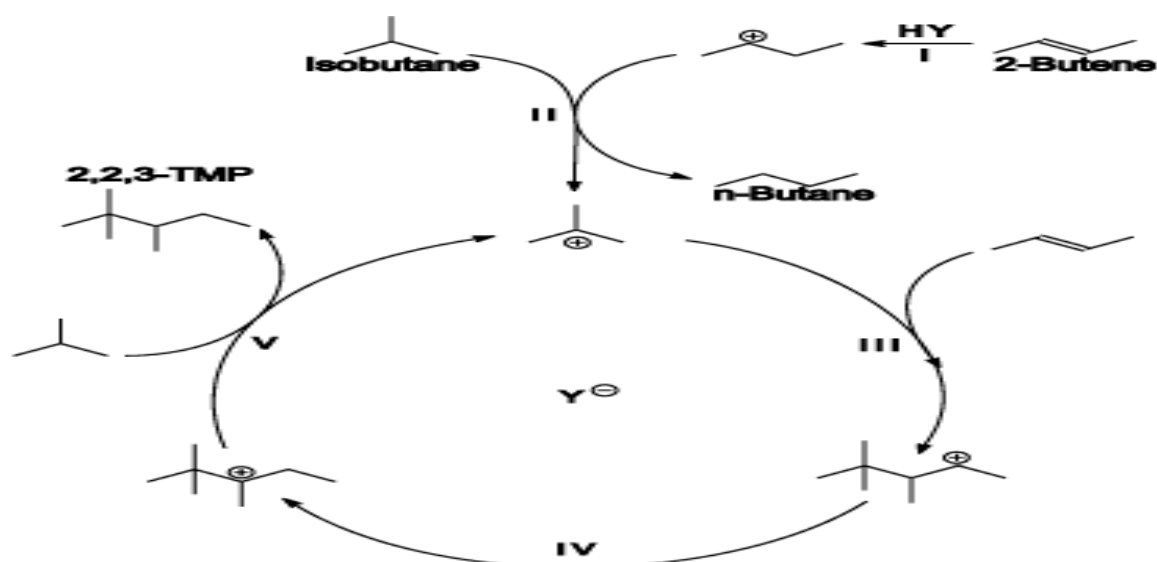
Advocates of sulfuric acid processes counter the above arguments for hydrofluoric acid processes with the following:

1. Additional equipment is needed for the hydrofluoric acid process to recover or neutralize the hydrofluoric acid in various streams. Such equipment includes the hydrofluoric acid stripper tower, hydrofluoric acid regeneration tower, and neutralization facilities for the several product streams. With sulfuric acid, the entire effluent hydrocarbon stream is neutralized.
2. Equipment is required to dry the feed streams to a few ppm water in hydrofluoric acid processes. Drying is beneficial but typically not required in sulphuric acid processes. Normally only feed coalesers are used to remove the free water that drops out of the chilled feed.
3. Additional equipment at increased cost is required for safety in a hydrofluoric acid unit. In some hydrofluoric acid plants, a closed cooling water system is required as a safety measure in the event of hydrofluoric acid leakage into the system. Maintenance costs and the amount of safety equipment in hydrofluoric acid processes are greater.
4. Capital costs for hydrofluoric acid processes are slightly more than sulphuric acid processes when the cost of hydrofluoric acid mitigation equipment is included.
5. Isobutane in hydrofluoric acid processes is not fully used for production of alkylate, since self-alkylation occurs to a higher extent when hydrofluoric acid is used as a catalyst.
6. There are greater limitations on obtaining alkylates with high octane numbers with hydrofluoric acid processes. This is particularly true if isobutylene is removed from the feed by an upstream MTBE or ETBE unit.
7. Safety and environmental restrictions limit the use of hydrofluoric systems in highly populated areas.

Reaction Mechanisms of Solid Catalyst Alkylation

According to Pam Pryor¹⁶, the alkylation of isobutane with 2-butene is a reaction normally catalyzed by Brønsted acids. The primary function of the acid system is to protonate the hydrocarbons to generate small concentrations of carbocations. Nevertheless, as the reaction begins it becomes autocatalytic due to a hydride transfer step as shown in Scheme 1.

¹⁶ Pam Pryor, Alkylation Current Events, 2000, STRATCO, Inc



Scheme 1. Isobutane/2-butene alkylation on HY zeolite.

The search for a solid catalyst to replace HF and H₂SO₄ in alkylation has been a long-standing challenge for chemists. Many materials are active for alkylation, but they show rapid deactivation, due to oligomerization, impairing the development of a commercial solid catalyst for this process. Some studies tend to overcome this problem, by working on process engineering solutions. According to some authors, the rapid deactivation of solid acid catalysts is due to a preferred adsorption of the olefins on the surface. This favors successive alkylation reactions, forming the oligomers, which do not desorb from the catalyst surface.

Zeolites are among the best solid catalysts tested in alkylation. One of the main features of the zeolites is their ability to catalyze hydride transfer. Notwithstanding, they still show a fast deactivation during alkylation. It has been recently shown that metal-exchanged zeolites can give rise to carbocationic reactions through the interaction with an alkyl halide. The metal cation acts as a Lewis acid site, coordinating with the alkylhalide to form a metal-halide species and an alkoxide bonded to the zeolite structure that acts as an adsorbed carbocation. It is not completely clear however, that ionic reactions on zeolites take place directly through the involvement of alkoxides, or there occurs a rapid equilibrium between alkoxides and free carbocations.

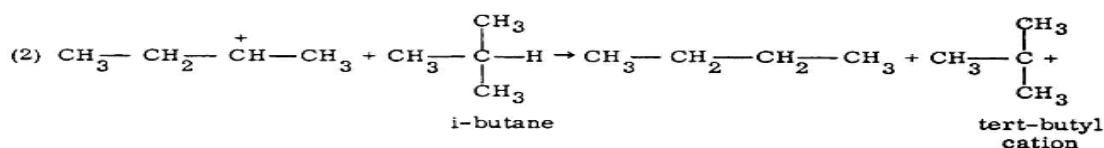
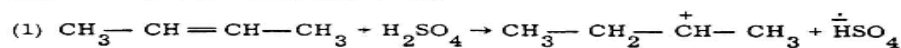
Research in the area of a solid catalyst for alkylation has been ongoing for many years. Numerous patents exist for different catalysts, catalyst supports, and processes. Several of the current preferred solid catalysts use a salt of HF: either boron trifluoride (BF₃) or antimony pentafluoride (SbF₅). Since every alkylation process produces heavy polymers, solid catalysts have the tendency to foul quickly. Therefore, solid catalyst processes have two major hurdles to overcome: *catalyst life and catalyst regeneration*. Several companies are engaged in active research in this area, but no one has yet commercialized a new alkylation technology. Table 2 summarizes the level of work in this area to date.

Table 2 Solid Alkylation Catalyst Research Status

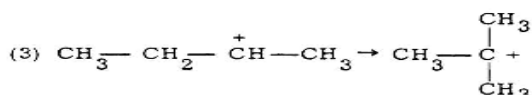
| | Catalyst Type | Project Status |
|--------------------|---|-----------------------|
| Catalytica | BF ₃ /Alumina | Abandoned |
| CR&L | SbF ₅ /Silica | Abandoned |
| Haldor Topsoe | Triflic | Continued Research |
| IFP | Promoted H ₂ SO ₄ /Silica | Abandoned |
| Kerr McGee/Chevron | AlCl ₃ | Abandoned |
| Mobil | BF ₃ /Zeolites | Continued Research |
| UOP | Carbon Supported HF? Looking for commercial partner | |
| | Zeolites? | |
| Lummus/AKZO | Unknown | Developmental |

The mechanism of liquid acid catalyzed reaction is shown below.

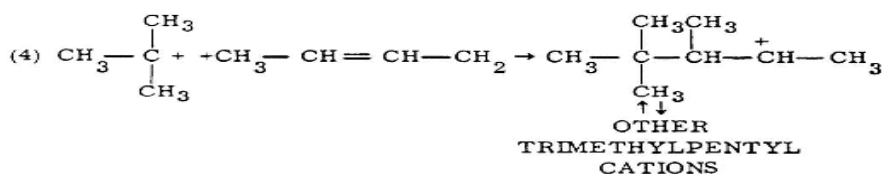
Initiation to form tert-butyl cation:



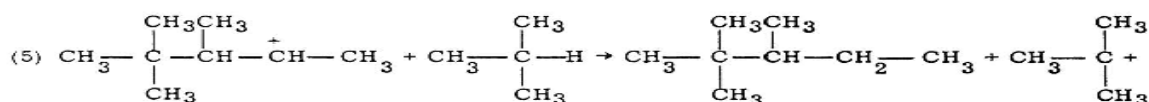
sec-butyl ion may isomerize instead of forming cation as in reaction (2):



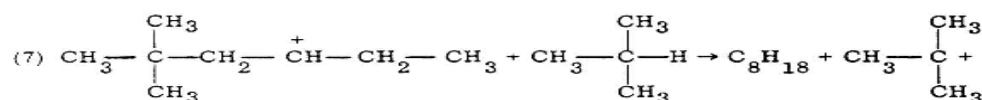
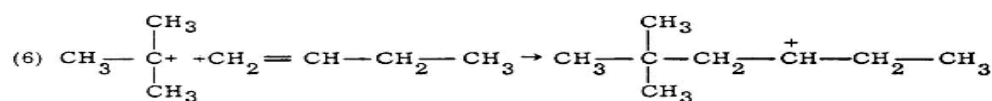
Reaction of tert-butyl cations with 2-butene:



Reaction of trimethylpentyl cations:



Formation of dimethylhexanes:



The formation of a new tert-butyl cation continues the chain.

Some of the latest findings of the chemistry of alkylation are reported¹⁷. The compounds: 1-butene, 2-butenes, and propylene generally react to a large extent first with the acid, and especially H₂SO₄, to form isoalkyl esters. These esters later decompose to free an olefin and the acid.

Table 3. Operating conditions for H₂SO₄ and HF alkylation¹⁹

| Process Catalyst | H ₂ SO ₄ | HF |
|----------------------------------|--------------------------------|-------|
| Temperature °C | 2-16 | 16-52 |
| Isobutane/olefin feed | 3-12 | 3-12 |
| Olefin space velocity, vo/hr./vo | 0.1-0.6 | |
| Olefin contact time, min | 20-30 | 8-20 |
| Catalysts acidity, wt % | 88-95 | 80-95 |
| Acid in emulsion, vol % | 40-60 | 25-80 |

¹⁷ Ipatieff, V.N and L.Schmerling (1948): Advances in Catalysis, Vol.1. Academic Press, new York, Pp 27-63.

Both sulfuric acid and hydrofluoric acid catalyzed alkylations are low temperature processes. Table 3 gives the alkylation conditions for HF and H₂SO₄ processes. One drawback of using H₂SO₄ and HF in alkylation is the hazards associated with it. Many attempts have been tried to use solid catalysts such as zeolites, alumina and ion exchange resins. Also strong solid acids such as sulfated zirconia and SbF₅/sulfonic acid resins were tried. Although they were active, nevertheless they lack stability¹⁸. No process yet proved successful due to the fast deactivation of the catalyst.

Table 4 below, for the purpose of comparison shows those attractive properties of alkylates as they appeal to refiners vis a-vis other blending components.

Table 4 Gasoline Blendstocks and Their Typical Properties²¹

| | Alkylate | FCC Naphtha | Reformate | Poly Gasoline |
|--------------------|-----------|-------------|-----------|---------------|
| Aromatics, LV% | 0 | 29 | 63 | 0 |
| Olefins, LV% | 0 | 29 | 1 | 95 |
| Sulfur, ppm | 16 | 756 | 26 | 75 |
| T50, °F (°C) | 216 (102) | 220 (104) | 256 (124) | 236 (113) |
| T90, °F (°C) | 289 (143) | 366 (186) | 334 (168) | 346 (174) |
| Driveability Index | 1134 | 1223 | 1299 | 1251 |
| RON | 93.2 | 92.1 | 97.7 | 94.4 |
| MON | 91.1 | 80.7 | 87.4 | 81.9 |

Alkylate is an ideal blendstock, having negligible amounts of toxics and ozone precursors and high RON and MON values. The driveability index of alkylate (1134) with low sulphur 16ppm stays consistently below the limit of 1200 currently proposed by the American Automobile Manufacturers Association (AAMA).

Comparison of H₂SO₄ and HF Alkylation Processes

Direct comparison of the two acid catalysts is not straight forward since each acid has advantages and disadvantages. For instance, some differences in alkylate quality occur when different C₄ olefin are used. For processes using sulphuric acid, a slightly better or equal alkylate quality is obtained when using 2-butenes or 1-butene, respectively, while isobutylene is the less preferred olefin feed. When HF is used as catalyst, 2-butenes are the preferred olefin feed, followed by isobutylene, while 1-butane produces an alkylate of lower quality. Higher alkylate quality has been reported with 1-butene and HF by working at high temperatures, but in the case of 2-butene and isobutylene, an alkylate of lower quality is produced. Less 1-butene isomerization occurs with HF as catalyst, and higher amounts of the less desirable dimethylhexanes are obtained. The octane number of alkylate using different olefin is given below:

¹⁸ Jacobs Consultancy Inc, Water Pollution Prevention Opportunities in Petroleum Refineries. The Washington State Department of Ecology, November 2002. Ecology Publication No 02-07-017.

Table 5. Comparison of Alkylates of the two Acid Catalyzed Processes with Olefin Feeds¹⁹

| Olefin feed | Octane number of alkylate using | |
|-------------|---------------------------------|-------|
| | H ₂ SO ₄ | HF |
| Propylene | 88-89 | 91-92 |
| Isobutylene | 91-92 | 93-95 |
| 1-Butene | 95.7-97.7 | 87-89 |
| 2-Butenes | 96-98 | 96-98 |

The pressure of propylene in the olefin feed has different effects when H₂SO₄ or HF is used as a catalyst. Table 5 shows among other things that, in an HF unit, the alkylate quality obtained from propylene is relatively good (91-92 RON), but isobutene consumption increases and relatively high amounts of propane are produced by hydrogen transfer reactions. A lower quality alkylate is produced with H₂SO₄ as catalyst (88-89 RON); however, no propane is produced and isobutane consumption is decreased.

With respect to the costs, the impact of the cost of the catalyst is much higher when using H₂SO₄ (about 30 percent) than HF (about 5 percent). In order to be competitive, the presence of an acid regeneration plant close to the H₂SO₄ alkylation unit is required.

Concerning separation costs, these are generally greater in HF processes due to several reasons. First, more isobutane has to be recycled (no isobutene is flashed in the reactor), with the exception of the UOP process with two reactors in series, and therefore bigger deisobutanizers with more energy requirements are used. Second, if propylene is present in the olefin feed, a depropanizer has to be used to prevent build-up in the reactor. On the other hand, although the acid regenerator is small, the safety device employed in the unit, as well as the separation of HF and fluorine containing compounds from the streams leaving the unit, have to be considered.

Finally, when using these types of acid as catalyst, safety concerns become very important. Both types of units have similar potential degree in respect to conditions that favour fires and explosion of hydrocarbon-air mixtures. However, significant differences arise when the acids are evaluated. The HF dangers can be reduced by reducing the acid inventory in the plant. This could be accomplished by the use of centrifuges to separate the acid instead of the settlers (or decanters). Smaller reactor or heat exchangers could be employed, or improved heat transfer could be realized, for example, by increasing the flow rates in heat exchangers.

Operating costs depend greatly on the specific operating conditions used but are estimated to be similar in many cases for both plants, if the regeneration acid plant and safety equipment are not considered. Capital costs were estimated to be similar for both H₂SO₄ and HF plants based on studies carried out in the early 1980s; however, this estimation did not take into account either the costs of an H₂SO₄ plant to regenerate the acid or the additional safety equipment required in today's HF units²⁰.

¹⁹ Kranz, K and David C, Graves (1998): Olefin Interactions in Sulfuric Acid Catalyzed Alkylation, paper presented at 215th National Meeting, American Chemical Society Dallas Texas, March 29th to April 1998.

²⁰ U.S Environmental Protection Agency (August, 1996) Study of Selected Petroleum Refining Residues, Industry Study Part 1 Washington DC, 20460.

Interactions between normal and iso-olefins occur in sulfuric acid alkylation and can affect acid consumption, octane, or both. The major points include:

- Non-linear trends are common with propylene and other olefins. When propylene is blended with butenes containing isobutylene or pentenes containing isopentenes, the effect on acid consumption and octane is nonlinear.
- Isoolefins appear to help react the stable propyl sulfates. Therefore, a propylene/mixed butene feed will show different trends than a propylene/MTBE raffinate feed.
- Lowered acid consumption and octane with propylene and pentenes. A large decrease in the sulfuric acid consumption can be seen when propylene and pentenes containing isopentenes are combined. Separation of the propylene from the pentenes can improve the octane. Different trends would be expected with propylene/TAME raffinate feed.
- Interaction between isobutylene and butenes. Part of the decrease in octane between normal butene and mixed butene feeds is due to this interaction.

Conclusions and Recommendations

When using these types of acid as catalyst, safety concerns become very important. Both acids are dangerous when contacting a person's skin, but HF is considerably more so. With respect to the acid leaks, H₂SO₄ leaks are generally limited to the surroundings, but when HF leaks occur, the acid is quickly dispersed from the release point over several miles, due to its high volatility. Several designs are used, using either of the catalysts. The most suitable alkylation process for a given refinery is determined by economics, especially with regard to the costs of acid purchase and disposal²¹.

Separate alkylation of normal butylene and isobutylene can improve alkylate octane.

Alkylate quality and operating costs can often be improved when the different olefins or olefin isomers are alkylated separately. Reacting different olefin feeds in separate reactors can offer savings in sulfuric acid consumption and improvement in alkylate quality by

- 1) Optimizing conditions for each olefin or pairs of olefins,
- 2) avoiding the negative interaction between olefins on alkylate quality and
- 3) combining or separating the interaction of propylene from pentenes for improved acid consumption or octane.

Many different processing schemes are possible depending on available olefin feeds, the number of reactors, and the refiner's overall alkylation economic objective - reduced acid consumption, improved octane, or both²².

By optimizing the capacities of the existing plants, reducing the operating costs and developing new products from the existing facilities, and embracing new and safer technologies, particularly H₂SO₄ catalyzed alkylation process, the goals of satisfying Nigeria and the West African fuel needs can be met. The production, distribution and pricing of petroleum products have become a thorny issue. A country like Nigeria that produces an abundance of crude oil should not lack petroleum products to power and lubricate her economy. The epileptic behaviour of its crude oil refineries and the inefficient distribution network have made the availability of petroleum products very difficult for business and pleasure. Goods cannot be produced by industries at competitive prices and the quality of life is going down. Nigeria's investments in refining should be geared toward domestic and regional opportunities in products marketing.

²¹ Nilton Rosenbach jr, Claudio J.A Mota (2005): Isobutane/2-butene alkylation with zeolite Y without Broensted acidity. Journal Braz.Chem Soc Vol.16 (4) Sao Paulo.

²² Mukherjee, M and Nehlsen J (2007): Reduce alkylate costs with solid-acid catalysts. Hydrocarbon Processing Vol.86(10), Pp 110-114.

The following actions will help to alleviate these problems and achieve our growth objective:

1. Government should, as a matter of urgency, complete the reactivation of all the refineries in Nigeria. Government should then vigorously pursue the outright or partial immediate sale or lease of our crude oil refineries at the best competitive prices to competent investor-operators who must produce and flood Nigeria with competitively priced Nigerian petroleum products.
2. Nigeria should pursue a strategy that conceives the whole of West Africa as its captive market for petroleum products. Investment in regional refineries should be geared toward this objective. These refineries will process Nigerian crude oil.
3. Nigeria should take the bold initiative to establish joint ventures in refining, in emerging markets of East Africa, Namibia, India, etc.
4. Nigeria should assure a captive market for her crude oil by purchasing some equity in a number of refineries in different parts of the world, including far away locations like India, New Zealand, Australia and China.

To sustain growth in the Nigeria petroleum industry and the refining industry, we need to involve academicians in industrialization strategies and significantly increase the Nigerian content in all segments of the economy. There are institutional deficiencies in four main areas: the educational institutions, the professional cadre, the indigenous manufacturing and service industry and the capital market²³.

HF alkylation units require extremely high levels of maintenance to ensure safe operation. Accidents have, in some cases, convinced the refinery management to moth ball these units. Three separate accidents involving HF releases at US refineries occurred in a 5-month span during 2009, leading to prolonged shutdowns and investigations by the US Chemical Safety and Hazard Investigation Board, Washington²⁴.

Solid acid-catalyzed alkylation eliminates the hazard and costs associated with using and regenerating corrosive liquid acids such as HF. Solid acids have for many years promised safer and cleaner alkylation. The short lifetimes of most solid acids, however, have resulted in expensive processes with complex reactors and large catalyst inventories, making them uncompetitive with liquid acid technology. Competing with liquid acids requires new solid acids that are engineered for optimum performance, rather than selected from existing materials.

²³ Mukherjee, M et al (2007): Developments in Alkylation. *Hydrocarbon Engineering*, Vol. 12(7), Pp 25-28.

²⁴ Mukherjee, M and Nehlsen J (2006): Consider catalyst developments for alkylation production. *Hydrocarbon Processing*, Vol 85 (9), Pp 85-96.

APPENDIX

Driveability Index (DI)

Another area that the automakers are discussing is driveability. They would like to include a DI in the specifications for gasoline. Control of the DI, derived from T10, T50, T90 and oxygen content can also be used to assure good cold start and warm-up performance. The formula for driveability is shown below (for temperatures in degrees Fahrenheit):

$$DI = 1.5(T10) + 3(T50) + T90 + 8.5(\text{vol\% EtOH}) + 3(\text{vol\% MTBE})$$

The oxygen correction factor is required to correct for higher driveability demerits for oxygenated fuels as compared to all hydrocarbon gasoline. The automakers favor setting a minimum T50 of 170 and a maximum driveability index of 1160-1200. They claim that a driveability index above 1250 leads to poor combustion. Along with higher emissions, start stalls, maneuver stalls and other losses of power can occur.