

SPECIFIC
TECHNOLOGICAL PROCESSES

A Review in Linear Alkylbenzene (LAB) Production Processes in the Petrochemical Industry

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Abstract—Linear alkylbenzene (LAB) is a cost-effective and biodegradable intermediate in the production of detergents and surfactants. Recently, due to the spread of the Coronavirus and the high global need for detergent, the production of LAB is essential. Kerosene is the raw material of linear paraffin with high purity, which is finally converted to linear olefins by dehydrogenation. The linear mono-olefins react with benzene in the existence of the catalyst to produce LAB which is used to produce linear alkylbenzene sulfonate (LAS), as a biodegradable detergent. The main methods for the production of LAB, including HF and Detal processes were studied and compared with each other. In Detal method, many compounds such as zeolites and metal oxides have been used to make solid catalysts with selectivity, long life, economic efficiency and high safety. Nowadays, most LAB production units have used the Detal process. In this review, the production of LAB was investigated, the influential factors and the advantages, disadvantages and limitations of each method were also investigated. The product quality, process economics, sales market, and the quantitative and qualitative properties of LAB have also been investigated. Also, the exact mechanism of LAB production by HF acid was described.

Keywords: linear alkylbenzene, detal process, linear alkylbenzene sulfonate (LAS), linear olefins, biodegradable detergent and surfactant

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INTRODUCTION

Conventional soaps are sodium salts of fatty acids that result from the alkaline saponification of animal or plant triglycerides. They were used until 1940, when synthetic soaps became popular. These synthetic soaps replaced conventional soaps for household use because they were less expensive and more used [1]. LABs are the most important raw material used in the manufacture of detergents. The highest production of these substances was during the alkylation reaction of benzene with linear olefins employing homogeneous acid catalysts during the Friedel–Craft reaction. These catalysts cause corrosion in the devices and damage to the environment [2, 3]. Nowadays, solid acid catalysts that are not easily recoverable and do not have the disadvantages of homogeneous catalysts have received much attention. Alkylbenzene sulfonate forms the basis

of synthetic detergents, first obtained by Friedel–Craft benzene alkylation with 12-carbon paraffins, and the alkylbenzene sulfonate produced under these conditions had branch. The produced synthetic detergents were then acquired by sulfonation of benzene dodecyl with fuming sulfuric acid and neutralization with caustic soda or sodium carbonate. Dodecylbenzenes, although effective detergents, were not biodegradable by bacteria due to their branching into the environment and polluting the seas and water sources. In the early 1960s, in many European countries, Japan and the United States, alkylbenzene sulfonates were substituted for dodecylbenzene sulfonates [4]. Aromatic compounds are difficult to degrade in the environment and LAB is a derivative of aromatics [5–8]. Due to superior biodegradation, linear alkylbenzene sulfonates were substituted for branched dodecylbenzene sulfonates. In the late 1960s, the dodecylbenzene sulfonate was

largely replaced by LAS in the United States, Japan, and many European countries. In addition, in the late 1970s, with the installation of facilities worldwide, the capacity of alkylbenzene sulfonate increased linearly. LAB now accounts for almost the entire production of alkylbenzene sulfonates and its demand enhanced from 1 million metric tons per year in 1980 to 1.8 in 1990. The production capacity will reach about 2.4 million tons per year by 2000 [9, 10]. After experiments performed by researchers, it was found that linear alkylates could be easily decomposed. Since then, LAS has been commercially introduced as a surfactant, with annual production in the United States, Japan and Western Europe of approximately 7.7%. It was 1 million tons. Extensive studies have been performed on LAS and its degradability behavior and it was found that its ecological effects can be controlled by consumption today. The total capacity of LAB products was about 2.8 million tons in 2002. Production of LAB in the United States is currently more than a billion pounds a year, and global usage will grow at a rate of 3.6%, annually. It can also present specific challenges on a commercial scale; alkylation spatial selection is difficult to control. There is an important rise in market demand for 2-phenyl isomers, forming aromatic polyalkyl and tetralin products should be minimal [11, 12].

The technology of LAB has almost replaced the old branched alkylbenzene technology surfactants based on enhanced biodegradation and cost-effectiveness. Today, the method of choice is the creation of normal paraffin to normal olefin, followed by alkylation of benzene to form LAB. The method based on solid catalysts is developing to replace HF acid units slowly to guarantee environmental safety and expand the economy. Many materials such as clays, zeolites, aluminum chloride and various types of metal oxides, have been appraised for this process as solid acid catalysts. Currently, only Detal technology is commercialized. Significant progress is being made due to continuing important studies on the catalyst properties and reaction mechanism which improves catalytic selectivity, and long stability of these solid acids at profitable operational circumstances [13].

In this study, the Detal and HF methods in the production of LAB were described and compared with each other completely. The influence of operational variables at the industrial scale in the HF methods such as temperature, pressure, Benzene to olefine ratio, HF to hydrocarbon ratio and water content were investigated.

In addition, the advantages, weaknesses and restrictions of each method were respected. The product quality, process economics, sales market, and the quantitative and qualitative properties of LAB have also been explored.

AN OVERVIEW OF ALKYL BENZENE PRODUCTION TECHNOLOGIES

Many of the following methods have been used to produce LAB. Linear sections of 10 to 14 carbon paraffin must be separated from kerosene, and in this process, zeolites are used to separate linear from nonlinear paraffins. The adsorptions have been used in UOP-Molex, UOP-Iso Siv, Exxon- Ensoorb and GDR Parex processes. The Molex process is a liquid phase method that uses hydrocarbons as desorbent. UOP-Iso Siv is a vapor phase process that works with adsorbent hydrocarbons. The Exxon-enzorb and Parex processes work in the vapor phase and ammonia is used as a repellent. In each of these processes, paraffin is obtained with a purity of more than 98%, which is either converted to alkyl chloride and reacted with aluminum trichloride catalyst with benzene to produce LAB, or to produce olefins by reacting with benzene in the existence of a hydrochloric acid catalyst to produce LAB [14].

Proposed Routes for the Production of LAB

(1) Linear paraffins are chlorinated and monochloroparaffin is formed and then an aluminum chloride catalyst is used which causes alkylation of benzene with monochloroparaffin [15], this method was used in the early 1960s.

(2) First, linear paraffins are chlorinated and then hydrogen is dechlorinated, in which case olefins are formed. Finally, hydrochloric acid is employed as a catalyst for the alkylation of benzene with linear olefins.

(3) Cracking waxes are formed by the oligomerization of ethylene or separating larger olefins. Alkylation of these olefins with benzene in the presence of a hydrochloric acid catalyst results in the production of LAB, which has been used by Shell and Amco Company.

(4) Dehydrogenation of linear paraffins and production of olefins is another method. These olefins react with benzene and produce LAB in the presence of the HF acid catalyst. Unreacted paraffins are returned to the beginning of the process after separation by

Table 1. Global production of LAB

Method	Production percent
Chlorination and Alkylation	10
Dehydrogenation and alkylation	81
Olefine with high olefine alkylation	9
Total	100

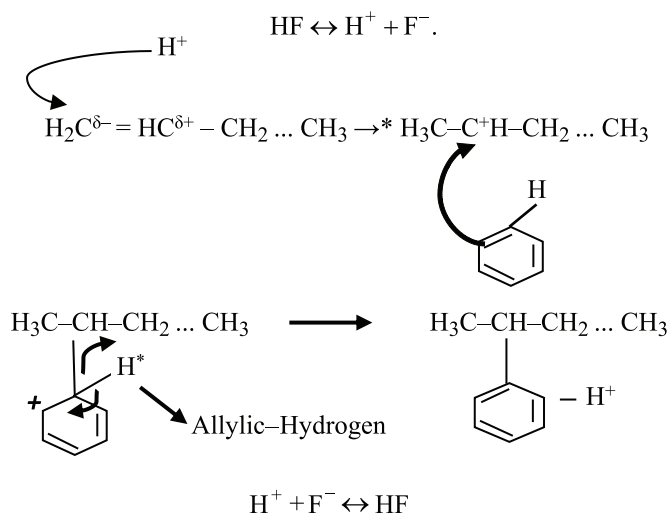
distillation. The UOP process is an example of this method. It became more common in the late 1960s due to the high quality of products and the economic benefits. The HF acid is one of the suitable catalysts with high recovery capability for alkylation reactions, but its disadvantage is that it is very corrosive and toxic and causes environmental pollution due to accidental or possible leakage, so they can be reduced to a minimum by taking the necessary measures and observing safety tips.

The HF acts as a homogeneous catalyst and it dissociated in the solution to a fluoride ion and a proton (positive ion of hydrogen), the H^+ has the main part in the catalytic alkylation reaction mechanism.



The activation energy between the reaction of benzene and olefine to produce LAB is very high, therefore high temperature and pressure is needed. So, by using an HF as a catalyst this activation energy decreased through forming carbocation intermediate

Scheme 1. The Friedel Crafts reaction mechanism in LAB production by HF catalyst.



and the reaction happened at mild operation conditions which can increase the safety of the process.

Usually, the olefine is asymmetric and the CH_2 groups are electron donors, therefore as can be seen in Scheme 1, the carbons of the double bonds have partial negative and positive charges which can be attacked by H^+ to produce carbocation as an active intermediate (*). In chemistry, the attack of chemical groups is from full electrons to fewer electron groups and the electrophilic substitution was happened by the attack of the cloud electron of the benzene ring to the positive carbon of carbocations. In an organic molecule, the hydrogen atom that is bonded to an allylic carbon is introduced as allylic hydrogen and its bonding to the molecule can be broken easily.

Finally, an allylic hydrogen ion was released from the complex and the LAB was produced as the desired product.

The separated H^+ reacted with fluoride ions once again and the catalyst (HF) was formed after the reaction.

(5) Due to the environmental problems of HF acid catalysts, the use of solid catalysts (Detal process) has succeeded, the use of this process has been increased since 1995. The Detal process involves the dehydrogenation of linear paraffins to olefins and the side reaction with benzene using a fixed bed catalytic reactor. During the early days of LAB production, chlorination of paraffin with alkylation under $AlCl_3$ was of particular interest, but after 1960 the dehydrogenation and HF alkylation method received more attention due to its economic benefits and high-quality products. Normal paraffin dehydrogenation methods are usually superior to other methods, due to the low cost of starting kerosene feed. About 81% of the produced alkylbenzene in the world is linear based on dehydrogenation and alkylation (Table 1).

The Detal method used a heterogeneous solid catalyst instead of fluoric acid and was started in 1995. Other LAB production methods are shown schematically in Fig. 1.

The new Detal process expanded with the UOP, PETRESA, and became a subsidiary of CEPESA Spain. The processes use an acid-stable substrate and a non-corrosive catalyst to replace HF acid. The catalysts of choice for the production of LAB have been fluoric acid since the first Pacol unit was put into production in 1968. Its high efficacy, excellent products and easy usage against $AlCl_3$ catalyst were the reasons for this success.

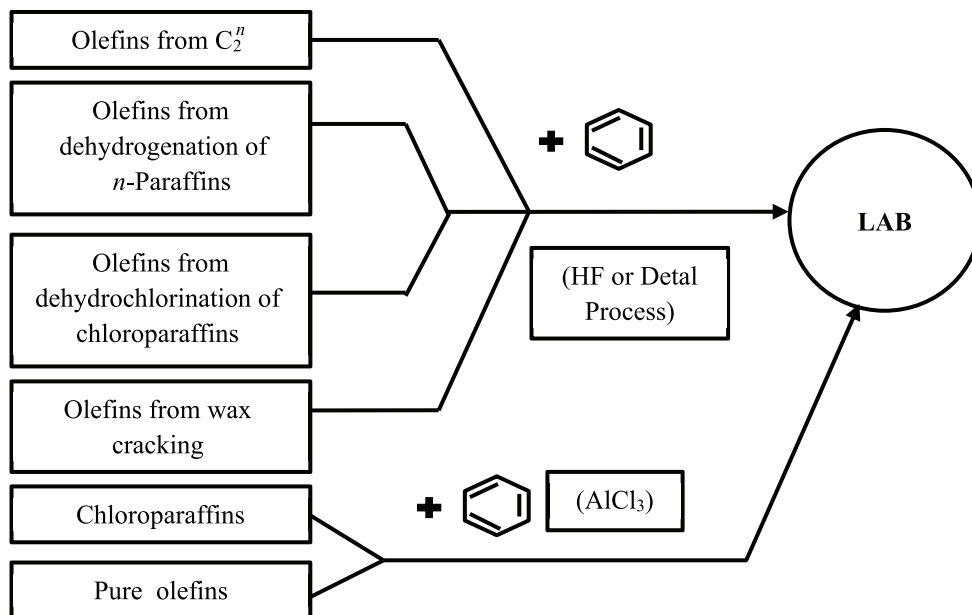


Fig. 1. Schematic of LAB production methods.

However, in both processes of catalyzing fluoric acid and AlCl_3 , the overall price of the company increases due to the transport of corrosive catalysts.

Therefore, the benefits of a heterogeneous catalyst are apparent. The key to an effective solid-bed alkylation method is a catalytic recovery that is selective, active, and stable throughout the operation. The UOP was effective

in improving solid catalysts for benzene alkylation with linear olefins for the production of LAB. The diagrams in Fig. 2 show the important difference between HF and Detal processes.

The diagram in Fig. 3 shows a LAB composite diagram showing Pacol and Defain in detergent alkylation units. This design remains unchanged for

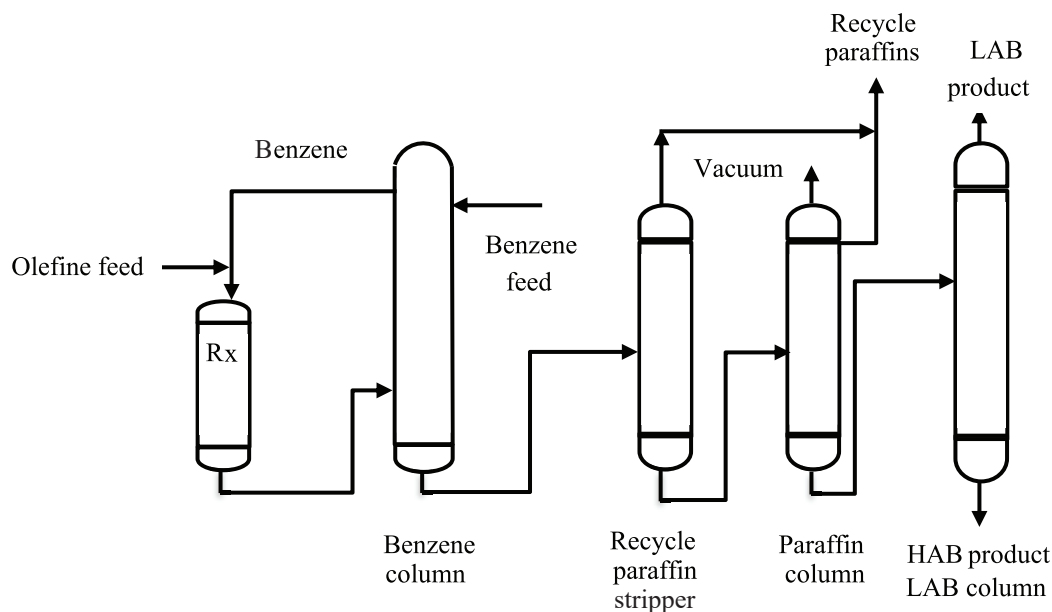


Fig. 2. Schematic of the Detal production process.

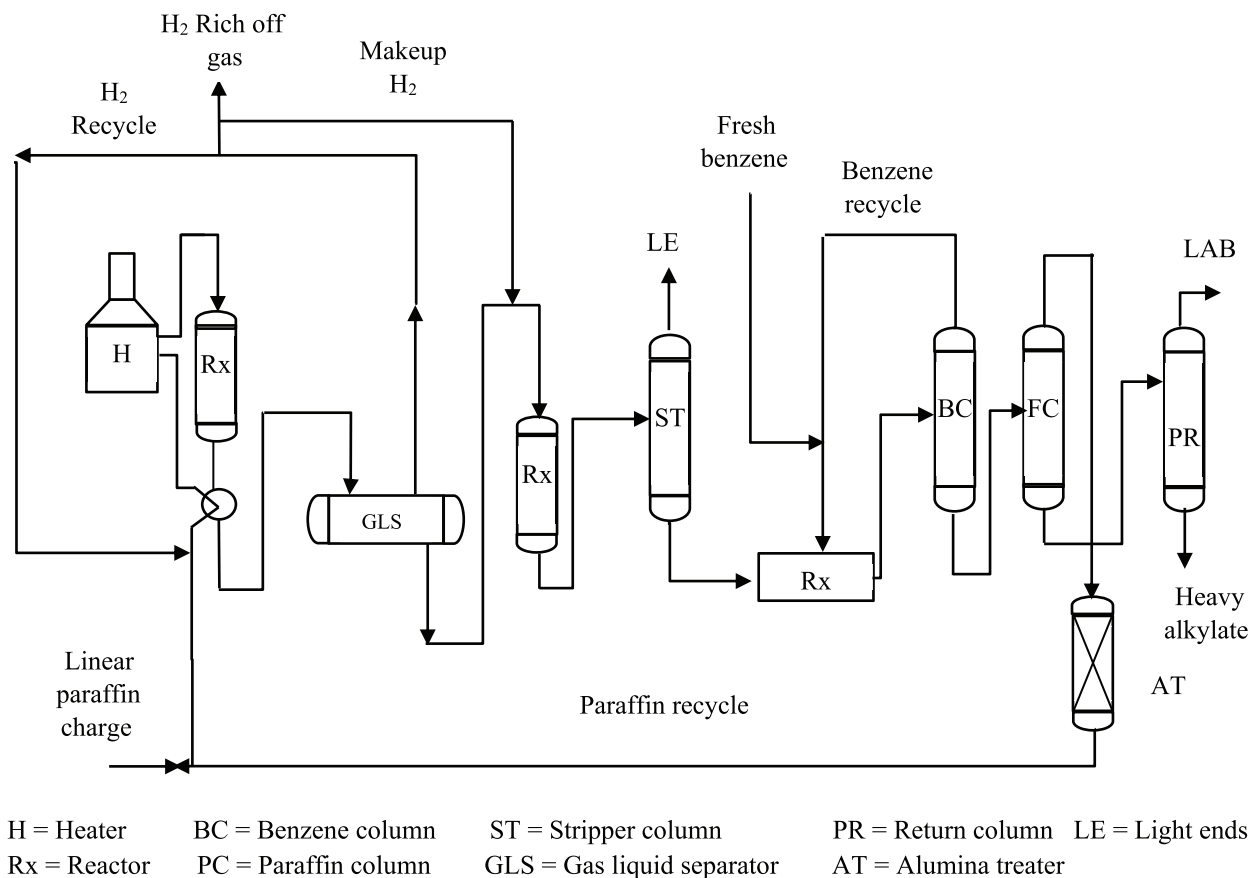


Fig. 3. Linear composite diagram of alkylbenzene production.

Pacol and Defain, HF acid, solid catalysis and fixed bed alkylation unit. In the HF acid alkylation process, the olefin feed from the Pacol–Defain units is mixed by recycling benzene and slowly cooled to mix with the HF acid. The reaction section includes an acid mixing and precipitating reagent. A portion of the fluorine acid phase is sent from the settler to the HF acid generator where the heavy by-products are moved again to increase the HF purity. The hydrocarbon phase moves from the acid settler to the distillation section where the residual HF acid, surplus benzene, unreacted normal paraffin, the heavy alkylates (HAB) and the LAB product are separated in distillation columns. Hydrofluoric acid and benzene are recovered for the alkylation reaction. Unreacted paraffins pass through an alumina reactor to remove fluoride and recover to the dehydrogenation unit. The hydrochloric acid process diagram shows that the hydrochloric acid is decomposed and transported, which requires the safe operation of the design. This

part creates a certain part of the project's investment price. In addition, in the dehydrogenation unit, nitrogen dioxide pollutants are also the product of the furnace output, which has been eliminated by researchers using a LECA-based manganese catalyst on a laboratory scale [16]. In the Detal scheme, the olefin feed is mixed with makeup and recycled benzene and streams in a fixed bed reactor whose catalyst is solid. The reaction occurs in the intermediate state in the liquid phase. The product of this reagent goes directly to the distillation section, which is similar to the fluoride acid section, except that the fluoride acid stripping column and alumina coating are removed. The omitted section includes the fluoride acid reagent, the mixing reagent, the acid settler, the fluorine acid generator, and the connecting piping. Additionally, not all special equipment and metallurgy are needed for fluoride acid transfer, vapor neutralization, and disposal of neutralized products. Since hydrocarbons including paraffin, olefin, benzene

and alkylbenzene are transported in the Detal process, only the carbon steel structure is employed. The monel parts and special pumps used in the fluoride acid service are then removed. Research on Detal catalysts shows that diolefins and other impurities, especially aromatics, which come from the Pacol hydrogenation unit, significantly affect the activity and ability of Detal catalysts and the quality of LAB. Therefore, one defining process unit must convert all diolefins to mono olefins. In addition, advanced UOP technology is used to eliminate aromatics from the alkylation feed. In the alkylation unit, these aromatics are usually alkylated with olefins to produce heavy alkylate as a by-product. The elimination of aromatics has two profits: increasing the efficiency of LAB in the olefin unit and improving the activity of the Detal catalyst.

Product Specifications of Alkylbenzene Produced by Different Processes

Usually, the manufacture of LABs from olefins and benzene commercially employing Lewis acid catalysts has been liquid HF acid. The use of fluoric acid typically produces about 17–18% of 2-phenyl alkanes. Lately, UOP/CEPSA reported that the Detal process for the manufacture of LAB uses a solid acid catalyst [17]. During the same period, several articles and patents were used to describe the synthesis of LAB employing a wide range of solid acid catalysts. Many of these solid acids produce more 2-phenyl alkanes than other methods.

Product quality. Table 2 compares the product characteristics of LAB for the two systems of HF and Detal process. The quality of the two products, HF and Detal, is similar, but the LAB produced from the Detal units is more linear, and the double bond compounds are less resulting in less heavy alkylates. Both products result in a small amount of tetralin in LAB, although the Detal process has a lower amount of tetralin compared to the HF process. As shown in Table 2, the color of the Colet from the 5% alkylbenzene sulfonate solution derived from the Detal is specifically less than the LAB obtained by the HF method. The most obvious difference between the HF and Detal method is the higher content of 2-phenylalkane in Detal method, which makes the LAB to be better sulfonated. The product derived from Detal becomes cloudy at a lower temperature and is less sensitive to density than the product of HF.

Economics. A comparative economic analysis was performed to produce 80 000 million tons per year of

Table 2. Comparison of different LAB production methods

Features	Detal process	HF process
Linearity, %	94–95	92–93
Specific weight	0.86	0.86
Bromine index	<15	15<
Color say bolt	>30	30>
Water content, mg/L	<100	100<
Tetralin, wt %	0.5<0	1.0<
2-Phenyl alkane	25>	18-15
LAB, wt %	95	93
Colet color Index in alkylbenzene sulphonate (5%)	10–30	20–40

LAB using the Detal or fluoric acid process. The size of the equipment for 8000 h per day was assumed to be proportional to the effective production of a capacity of 240 meters per ton per day. The rising price for a compound based on the HF process was estimated at \$56 million. For another similar combination that used the Detal process, a price of \$45 million was assumed. The economic analysis is concise in Table 3. The products in this table have a molecular weight of 240.

By-products include 95% molar hydrogen, light products, heavy alkylates, and HF acid containing products. In Detal process, the operational costs are reduced by lack of fluoric acid and therefore lack of corresponding neutralization facilities for acidic wastewater. The current technology economics of Detal and hydrofluoric acid are fully described. For a LAB unit of 80,000 tons per year, cost estimates for Detal and HF systems were \$67 million and \$72 million, respectively. Factory fixed investment has decreased by approximately 15%.

Sales market. The gradual development in demand of LAB varies in other geographical areas. The use of LAB in different geographical areas in the 1980s and 2000s are summarized in Table 4.

CATALYSTS USED IN THE ALKYLATION PROCESS

The use of HF to catalyze the reaction of non-LAB production began in 1960, so in 1968 it was first used to produce LAB from linear alkanes in the Pacol unit.

Table 3. Economic analysis of the Detal and HF process

Raw material	Unit of cost (dollars)	Detal process per million tons of alkylbenzene linearly (Amount)		Hydrofluoric acid process linear per million tons of alkylbenzene (Amount)	
		Dollar	Dollar	Dollar	Dollar
Linear Paraffin	480	352	0.78	350	0.78
Benzene	300	100	0.33	99	0.33
Side Product		21		20	0.33
Catalyst and chemical material		28		21	
Utilities					
Electricity (KWh)	0.05	14	281	14	283
Cooling water(m ³)	0.02	1	24	2	81
Consumed fuel (million M3)	3.74	27	3.04	25	2.86
Fixed cost					
Cash cost of LAB production		548		545	
Cash flow (million dollars) Alkylbenzene linearly at \$850 per ton		24.2		24.4	
Estimated installation cost (million dollars)		50.6		70.1	
Simple repayment (year, fixed investment)		1.9		2.2	

The LAB is obtained by benzene alkylation through the Friedel–Craft catalyst in the presence of aluminum chloride or HF [20], and linear alkenes are obtained by dehydrogenation of alkanes. The two alkylation processes are performed by HF, but most alkylation in liquid products is performed by the Friedel-Craft method in the presence of AlCl₃. The LAB produced will not be the same but will have different isomers. In the case of AlCl₃ as a catalyst, 25–30% of 2-phenyl isomer and 15–22% of 3, 4, 5, 6-phenyl isomers are produced [19].

Table 4. The use of LAB in different geographical areas

Region	Consumption of LAB (1000 MTA)	
	2000	1980
Europe and the former Soviet Union	470	415
Africa	140	35
Middle East	170	30
Asia	800	280
America	820	290
Total	2400	1050

Many solid catalysts are used for the alkylation process, but not all of them have the selectivity to produce the desired product and stability under reaction conditions. Solid acid catalysts can be used for the production of LAB and have selectivity, long life and stability under reaction conditions [20]. Studies have been done on different solid catalysts such as clay, alumina and magnesium silicate. The effect of different zeolites on the process has been investigated and the size of the zeolite has an important effect. The use of solid acid catalysts has developed to include the deposition of aluminum chloride on hexagonal mesoporous silicon with cavities of 1.6 and 2.4 nm. The aluminum chloride supported on a base was much more active than the baseless type. One of the most important problems of solid catalysts is the possibility of forming carbon deposits due to possible diolefine present in the feed on the active pores of the catalyst and as a result of catalyst poisoning [21].

METHODS CURRENTLY USED TO PRODUCE LAB

The alkylation process typically in a homogeneous catalytic system using acids as catalysts causes

problems including toxicity, corrosion of equipment, low selectivity, difficulty separating the product and production of waste materials. In addition, the toxicity and corrosiveness of these acids cause problems during transportation, and their storage and disposal. On the other hand, separating these acid catalysts from reaction products is associated with high energy consumption. Thus, the use of solid and environmentally friendly catalysts as an alternative to these acidic compounds has been considered [22]. The methods currently used are either based on liquid catalysts such as aluminum chloride and fluoric acid, or solid catalysts. The most important commercial process for the production of LAB is the Detal method proposed by the UOP. This process combines with the dehydrogenation process, and the olefin produced is mixed with makeup and recycled benzene and enters the catalytic reaction bed containing the acid solid catalyst. In this process, carbon steel can be used instead of Monel equipment used for HF acid. To increase the yield in the Detal process, the aromatics in the paraffin feed stream that cause catalyst poisoning must be removed and all selective hydrogenation must be converted to mono olefin by selective hydrogenation because the dyes react together under reaction conditions to produce heavy compounds that cause deposition on the catalyst surface [23].

LAB MARKET IN THE WORLD AND THE REGION

The world production capacity of LAB in 2018 was 1.4 million tons. An average increase of 2.2% in production capacity is predicted for 2018 to 2030. On the other hand, on average for 2020 to 2027, growth in global demand is estimated at 4.7 percent. Last year (2020), the growth rate was estimated at 2.7 percent, which has increased due to the occurrence of the Corona (Covid-19). In the global LAB market, the top 5 players are Sepsa (570 000 tons), Sasul (360 000 tons), Jin Tong (350 000 tons), Fushun (280 000 tons) and Sinopec (200 000 tons), which have about 46% of the product. The Middle East has about 20% of the world's production capacity. The regional producers of this product are mainly Saudi and Qatari companies. Farabi Petrochemical located in Saudi Arabia with a nominal annual capacity of 140 000 tons is one of these companies. The company will soon initiate the 120 000 ton project. A company at its petrochemical plant in Mesaieed, Qatar produces 100 000 metric tons per annum of linear alkyl

benzene with Detal technology, 80 000 metric tons per year of normal paraffin, and 36 000 metric tons per year of benzene. Some of these reported data are different from the reported data in Table 5 because the data in Table 5 is derived from design values. Before 1994, the country's need for this strategic product was met through imports. Iran Chemical Industries Investment Company was put into operation on June 1, 1994, with a capacity of 50 000 tons.

PROPERTIES OF LINEARLY PRODUCED ALKYL BENZENE

Bromine Index

The number of milligrams of bromine atoms that can react with 100 mg of the sample is called as bromine index. The bromine index is one-thousandth of the bromine numbers. Since bromine does not react with benzene ring double bonds (due to high stability and resonance) and only reacts with possible double bonds in the alkyl group attached to the LAB, bromine index is a measure of the double bonds in the linear chain. This index is normally less than 15 in the solid and liquid catalyst process, which is desirable. The bromine index is very effective on the price of the product.

Color Index

The color of compounds has a direct relationship with the presence of chromophore, auxochrome and resonance groups in the compounds. Since there is no chromophore and auxochrome in the structure of LAB, the effect of resonance on the color is very effective. As the double bonds in the chain increase, the resonance increases and the product becomes more colorful.

EFFECTIVE OPERATIONAL VARIABLES IN THE HF ALKYLATION PROCESS

Temperature. Temperature control is significant since the reaction of an olefin with benzene and the production of LAB in the presence of HF catalyst and is associated with entropy loss, so a coolant is used. As the temperature rises, the possibility of corrosion increases. The reaction temperature is kept at about 38°C.

Pressure. The investigation of the pressure requires further studies, but the pressure must be such that the reaction phase does not change. The effect of pressure on the effective collision rate between reactants needs further investigation.

Table 5. Production capacity of companies producing different LAB in the world

Company	Town, country	Capacity (multiplied by 10 ⁻³)	Process
America Petroleum Refining	America, Egypt	50	Alkylation with fluoric acid
Bisotun Petrochemical	Kermanshah, Iran	55	Alkylation with fluoric acid
CEPSA Quimica	San Roque, Spain	220	The most important and the first company with Detal technology
Chemische Fabrik Wibarco	Ibbenburen, Germany	66	Alkylation with fluoric acid
Chevron Chemical	Gonfreville, France	100	Alkylation with Detal and fluoric acid
Deten Quimica	Camacari, Brazil	220	Alkylation with Detal
Emalab	Jebel Ali, Dubai	30	Alkylation with fluoric acid
Formosan Union Chemical	Lin Yuan, Taiwan	90	Alkylation with Detal and fluoric acid
Fushun Petrochemical	Fushun, China	200	
Gulf Farabi Petrochemical	Jubail, Saudi Arabia	70	Alkylation with fluoric acid
Huntsman performance products	Chocolate Bayou, Texas, US	180	Alkylation with Detal
Indian Oil	Baroda, India	75	
Iran Chemical Industries Investment	Esfahan, Iran	75	Alkylation with fluoric acid
Isu Chemical	Ulsan, South Korea	190	Alkylation with fluoric acid
Jin Tung Petrochemical	Nanjing, China	200	Alkylation with Detal
Lukoil Neftochim Burgas	Burgas, Bulgaria	5	Alkylation with fluoric acid
Nippon Petrochemicals	Kawasaki, Japan	45	Alkylation with fluoric acid
Nirma	Baroda, India	110	Alkylation with fluoric acid
OHIS	Skopje, Macedonia	18	Alkylation with fluoric acid
Petresa Canada	Becancour, Canada	120	Alkylation with Detal
Qatar Petroleum	Mesaiced, Qatar	100	Alkylation with Detal
Quimica Venoco	Guacara, Venezuela	135	Alkylation with Detal
Reliance Industries Ltd. (RIL)	Patalganga, India	115	Alkylation with fluoric acid
Repsol	Ensenada, Argentina	50	Alkylation with fluoric acid
Sasool	Augusta, Italy	220	Alkylation with Detal
Sasol	Louisiana, US	125	Alkylation with Detal
Sinopec Jinling - Petrochemical	Nanjing, China	100	Alkylation with Detal
Tamilnadu petroproducts	Manali, India	100	Alkylation with fluoric acid
Unggul Indah Cahaya	Merak, Indonesia	210	Alkylation with Detal
United Joint Stock Co. for Petrochemical Industries	Damascus, Syria	40	Alkylation with fluoric acid
America Petroleum Refining	America, Egypt	50	Alkylation with fluoric acid

Table 5. (Contd.)

Company	Town, country	Capacity (multiplied by 10 ⁻³)	Process
Bisotun Petrochemical	Kermanshah, Iran	55	Alkylation with fluoric acid
CEPSA Quimica	San Roque, Spain	220	The most important and the first company with Detal technology
Chemische Fabrik Wibarco	Ibbenburen, Germany	66	Alkylation with fluoric acid
Chevron Chemical	Gonfreville, France	100	Alkylation with Detal and fluoric acid
Deten Quimica	Camacari, Brazil	220	Alkylation with Detal
Emalab	Jebel Ali, Dubai	30	Alkylation with fluoric acid
Formosan Union Chemical	Lin Yuan, Taiwan	90	Alkylation with Detal and fluoric acid
Fushun Petrochemical	Fushun, China	200	
Gulf Farabi Petrochemical	Jubail, Saudi Arabia	70	Alkylation with fluoric acid
Huntsman Performance Products	Chocolate Bayou, Texas, US	180	Alkylation with Detal
Indian Oil	Baroda, India	75	
Iran Chemical Industries Investment	Esfahan, Iran	75	Alkylation with fluoric acid
Isu Chemical	Ulsan, South Korea	190	Alkylation with fluoric acid
Jin Tung Petrochemical	Nanjing, China	200	Alkylation with Detal
Lukoil Neftochim Burgas	Burgas, Bulgaria	5	Alkylation with fluoric acid
Nippon Petrochemicals	Kawasaki, Japan	45	Alkylation with fluoric acid
Nirma	Baroda, India	110	Alkylation with fluoric acid
OHIS	Skopje, Macedonia	18	Alkylation with fluoric acid
Petresa Canada*	Becancour, Canada	120	Alkylation with Detal
Qatar Petroleum	Mesaieed, Qatar	100	Alkylation with Detal
Quimica Venoco	Guacara, Venezuela	135	Alkylation with Detal
Reliance Industries Ltd. (RIL)	Patalganga, India	115	Alkylation with fluoric acid
Repsol	Ensenada, Argentina	50	Alkylation with fluoric acid
Sasool	Augusta, Italy	220	Alkylation with Detal
Sasol	Louisiana, US	125	Alkylation with Detal
Sinopec Jinling Petrochemical	Nanjing, China	100	Alkylation with Detal
Tamilnadu Petroproducts	Manali, India	100	Alkylation with fluoric acid
Unggul Indah Cahaya	Merak, Indonesia	210	Alkylation with Detal
United Joint Stock Co. for Petrochemical Industries	Damascus, Syria	40	Alkylation with fluoric acid

Ratio of benzene to olefine. Since the alkylation reaction mechanism of Friedel Craft is an electron-friendly substitution, in this process, first, the HF acid predisposes the double bond of olefins to start the reaction (reduces the activation energy of the reaction), because olefins are asymmetric. There is a negative double bond on carbon, and in chemistry, the attack always takes place from a high electron to a low electron, ie the benzene ring attacks the double bond and eventually, LAB is produced. Since the alkyl group is electron-induced, the reaction product (LAB) is more susceptible than the reactant (benzene) to attack olefin-positive carbon. One of the problems of this process is polyalkylation and production of heavy alkylate products, which by selecting a high ratio of benzene to olefin, the production of unwanted product (heavy alkylate) is minimized. Increasing the amount of benzene to the extent that it does not cause pressure on the reaction part and does not impose high cost and energy to separate it in the distillation section, usually the molar ratio of benzene to olefin is considered to be about 10.

Ratio of acid to hydrocarbon. This ratio should be 70 to 30 by volume, ie the amount of circulating acid in the reaction should be almost twice the amount of hydrocarbons, about 90% of which is paraffin and 10% of which is an olefin, so that the hydrocarbon phase is immersed in the acid phase as emulsion droplets. Under these conditions, there is the highest contact between the catalyst and the hydrocarbon phase. If this ratio is reduced, the effective surface between the catalyst and the olefin is reduced and not all of the olefin double bonds are catalyzed by the acid, so the double olefin bonds combine to form heavy compounds, in which case the bromine index of the product usually increases.

Effect of the hydrocarbon phase flowrate entered to HF Alkylation unit. Since the volume of the reaction zone and the acidic part is constant and also the recycling acid in the system is almost constant and fewer changes are made on it. So, increasing and decreasing in the hydrocarbon flowrate can decrease and increase the residence time of reactants molecules, respectively. As the residence time of the reactants increases, the conversion percentage of the reactants increases, but the selectivity of the reaction and the production of the desired product decreases and the

manufacture of unwanted by-products such as heavy alkylates increases.

The effect of water on the reaction part. Water does not have a direct effect on the efficiency of the reaction, still, its amount in the reaction cycle should be a certain amount of about 0.3 to 0.5% by weight in the acid phase. This ratio should not be less than 0.1% by weight. Increasing this ratio facilitates the precipitation of the acid phase from the hydrocarbon phase, but increases the probability of corrosion in the system. Reducing this ratio interferes with separating the acid phase from the hydrocarbon phase in the precipitators.

Ratio of input feed to acid regeneration tower to the mass of LAB produced. Heavy acid-soluble hydrocarbons are produced as a by-product in the process. These compounds must be sent to the acid regeneration tower where the acid is separated and the heavy hydrocarbons with partial acid are sent to the appropriate tanks after neutralization. The amount of acid flow entering the acid regeneration tower indicates the purity of the acid. The ratio of input feed to acid-regenerating tower to the mass of the produced LAB is maintained between 0.5 to 1. The differences of alkylbenzene are linear along the carbon chain in the final product and the position of the benzene ring relative to the carbon chain. If the number of carbon atoms in the alkyl group is 12, the product is better. In addition to the lower investment cost and higher safety, the Detal process has other advantages such as higher 2-phenylalkane production, higher conversion and selectivity, sulfonated products with better color and regeneration of by products, compared to the HF acid process [24].

OTHER PARAMETERS

Current technology of commercial alkylbenzene. Current technologies for the production of LAB are based on solid acid or HF catalysts. Until now, there is only one commercially recognized technology using a solid acid catalyst, the second technology is being tested in India [25]. There is little information about this method, only that it may be based on zeolite. This system has not been fully marketed and is the only commercial process technology provided by UOP. Detal catalyst is a specific solid acid that has been produced specifically for this application [26]. So far, this technology has

two commercial units and is performed in conjunction with UOPs dehydrogenation method to produce linear olefins. The olefins feed and the recycled benzene are combined with the compensating benzene before entering the fixed bed reactor comprising the solid acid catalyst. The reaction in the liquid phase occurs in mild conditions to reach the desired product quality. Hydrofluoric acid stripping columns, settlers, plumbing and hydrofluoric acid equipment are removed. Also, carbon steel metallurgy can be applied due to the lack of liquid acid. To improve the performance and quality of the product, there are two additional components for the Detal unit. First, a Define unit is added for selective hydrogenation of diolefine to mono olefine (same as the HF technology) to increase the yield of alkylates. Second, a PEPTM aromatic removal unit is added to remove aromatic substances from the olefin feed stream. These aromatic substances will be alkylated in the Detal unit, which leads to faster inactivation of the catalyst and the low-quality product.

Product quality. Bromine index and sulfonation ability are the main criteria of product quality because they affect the price of the final product. The product with a high bromine index also creates a highly colored sulfonate that needs further refining. Recently, the regeneration of non-alkylbenzene components, especially tetralin regeneration and linear improvement, has become more important. Both of these parameters are related to the improvement of the biodegradation rate of the final product [27]. As shown in Table 2, the LAB product has a higher yield, higher linear percentage, an improved sulfonate color, and less tetralin by-product. It also has a higher 2-phenylalkane content, which increases the solubility in many formulations. All of these characteristics indicate that current Detal technology produces superior products to HF technology.

Advances in LAB alkylation catalysts. Since the first UOP detergent alkylation plant began in 1960, HF acid has been the alkylation catalyst for the production of branched alkylbenzenes. The same partially modified flow scheme has been used to produce LABs using linear olefins derived from the Pacol unit since 1968 [28]. The superior product quality, high efficiency, and ease of use compared to aluminum chloride technology led to its supremacy in alkylated complexes. It is possible to use conventional metallurgy to build,

easily separate the product and remove HF acid waste. Many acidic solids are active for the alkylation of benzene with different olefins. Though many catalysts are active, they commonly lack selectivity or stability depending on the processing time. An efficacious solid bed alkylation process needs a solid acid catalyst that is selective, active, regenerative, and stable over a long time to be cost-effective in comparison with HF acid. Several studies have been performed on clay, alumina or silica - alumina silicotonic acid and aluminum silicate or magnesium silicate [29]. Beyond these articles, due to the rapid deactivation or low quality of the product, not much effort has been made to investigate these materials. Zeolites have been extensively evaluated for the production of LAB. Another method to minimize corrosion in the liquid alkylation system includes the use of ionic liquids [30]. The Ionic liquids are mainly mixes of low melting point salts including pyridinium halides, imidazolium halides, or phosphonium halides. The active catalyst is produced by adding $AlCl_3$ or other Lewis acids. These are suitable catalytic systems because the product separates cleanly from the ionic liquid and is separated easily by reusing the acidic phase. So far, more than 99% of Decen to phenyl decan conversion with more than 99.5% recyclable ionic liquid has been achieved. One of the main technical obstacles of this technology is the ability to regenerate ionic liquid after a long time in the flow and the instability of these systems in the existence of water. The need to rinse the alkyl product to remove ionic liquids or trace chloride must also be determined. So far, none of the above systems have been marketed. Generally, poor product quality, poor economic performance and long-term instability of the catalyst have always been a problem [8].

Environmental aspects of LAB production in the petrochemical industry. Since benzene is one of the carcinogenic compounds according to the World Environment Organization, so in case of discharge to the company's wastewater systems, treatment of wastewater containing benzene derivatives is necessary. Classical methods for treating effluents containing LAB are not suitable because these effluents are biodegradable and classical methods basically transfer the pollutant from one phase to another and do not substantially degrade the pollutant. Therefore, advanced oxidation methods based on the active hydroxyl radical are used [31, 32].

CONCLUSIONS

One of the most important intermediates for synthetic detergents is LAB. The branched alkylbenzenes previously used have been completely replaced by LAB due to their non-degradable nature. Today, in the process of producing LAB from benzene and olefins, the use of solid catalysts has become much more common than HF acid. Various solid catalysts including zeolites, various metal oxides and aluminum chloride supported on the base have been studied but they usually lacked the necessary properties such as high efficiency, stability and selectivity and so far, only the Detal process has been successful. The effect of various operational variables such as acid to hydrocarbon ratio, benzene to olefin ratio, the volumetric flow rate of feed inlet to reaction zone, ratio of feed inlet to acid regeneration tower to the mass of produced LAB, amount of water in reaction, effect of temperature and pressure in the HF process has been investigated.

In addition, the advantages, weaknesses and restrictions of each method were also inspected. The product quality, process economics, sales market, and the quantitative and qualitative properties of LAB have also been explored.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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