Production of linear alkylbenzenes

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Abstract

Linear alkylbenzene technology has almost completely replaced the older branched alkylbenzene technology for production of surfactants due to improved biodegradability and cost-effectiveness. The technology of choice today is dehydrogenation of *n*-paraffins to *n*-olefins followed by benzene alkylation to produce linear alkylbenzene. Solid acids catalyst-based systems are emerging to slowly replace hydrofluoric acid units in order to ensure environmental safety and improve economics. Numerous materials have been evaluated as solid acid catalysts for this alkylation process including zeolites, clays, various metal oxides, and supported aluminum chloride. At this time, only the UOP Detal technology has been commercialized. Because of ongoing fundamental studies on reaction mechanism and catalyst properties, significant progress is being made to improve the selectivity, catalytic stability, and long-term stability of these solid acids under commercial operating conditions. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Natural soaps are sodium salts of fatty acids obtained by alkaline saponification of triglycerides from either vegetable or animal sources. These natural soaps were prevalent until the 1940s when sodium alkylbenzene sulfonates became available. These synthetic surfactants had detergency characteristics that were superior to those of natural soaps. Additionally, the synthetic surfactants had a lower cost and a wider range of applications. This new surfactant replaced natural soaps in household laundry and dishwashing applications. The discovery of synthetic alkylbenzene sulfonates formed the basis for the detergent industry.

The first alkylbenzene sulfonates were obtained by the Friedel–Crafts alkylation of benzene with propylene tetramer. The tetramer is a mixture of C_{12} olefins.

As a result, the corresponding alkylbenzene sulfonate is highly branched. The detergent product is then made by sulfonation of the dodecylbenzenes with oleum or sulfur trioxide followed by neutralization with sodium hydroxide or soda ash. The active-detergent could then be formulated into the commercial product.

Although the dodecylbenzene was an effective detergent, it has slow rates of biodegradation in the environment. It became apparent that dodecylbenzene-based detergents were contributing to the pollution of lakes and streams by forming relatively stable foams. In the early 1960s, the linear alkylbenzene sulfonates were introduced. Due to its superior biodegradability, linear alkylbenezene sulfonates began replacing branched dodecylbenzene sulfonates.

Dodecylbenzene sulfonate was largely replaced by linear alkylbenzene sulfonate by the late 1960s in the United States, Japan, and many European countries. Furthermore, by the late 1970s, linear alkylbenzene sulfonate capacity increased rapidly with facilities being installed around the world. Linear alkylbenzene

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now accounts for nearly all of the worldwide production of alkylbenzene sulfonates. The demand increased from about 1 million metric tonnes per year in 1980 to about 1.8 million metric tonnes in 1990. The production capacity is expected to grow to about 2.4 million metric tonnes annually by the year 2000.

2. Linear alkylbenzene technology overview

Several routes have been used for the production of linear alkylbenzene. First, C_{10}–C_{14} linear paraffins must be separated from kerosine or gas oil fractions. Adsorptive separation and recovery techniques conducted in vapor or liquid phase were developed. A variety of adsorbents and desorbents are applicable to this process. Since the mid 1960s, the use of 5-A zeolites has dominated as the adsorbent of choice. Commercial process technologies for this process include UOP^{TM} Molex^{TM} process, UOP^{TM} IsoSiv^{TM} (formerly Union Carbide) process, Exxon Ensorb process and the GDR Parex process. Molex^{TM} is a liquid phase process using a hydrocarbon desorbent that makes use of UOPs Sorbex^{TM} simulated moving bed technology. IsoSiv^{TM} is a vapor phase process operating with a hydrocarbon desorbent. The Exxon Ensorb and GDR Parex processes operate in the vapor phase with ammonia as desorbent.

The linear paraffins are recovered at >98% purity in each of these processes. The linear paraffins are converted into alkyl chlorides or olefins, and alkylating benzene with them produces linear alkylbenzenes.

Various technologies developed include:

- Chlorination of linear paraffins to form mono-chloroparaffin. Aluminum chloride catalyst is used to alkylate benzene with the mono-chloroparaffin. For example, ARCO Technology Inc. [1] has developed and commercialized this route.
- Chlorination of linear paraffins followed by dehydrochlorination to form olefins as the alkylating agent that has been used by a few companies. Shell's CDC (chlorination/dehydrochlorination) process is an example. Hydrofluoric acid is generally used as the catalyst for benzene alkylation with linear olefins.
- Wax cracking, alpha olefins from ethylene oligomerization, or linear internal olefins from

olefin disproportionation can produce olefins. Alkylation of benzene with these olefins is conducted using hydrofluoric acid catalyst. Companies that use these various routes include Albermarle (now Amoco), Chevron, and Shell.
- Dehydrogenation of linear paraffins to a mixture of linear olefins is another route to paraffin activation. The olefin-containing stream is used to alkylate benzene using HF acid catalyst. The unconverted paraffins are then recycled back to dehydrogenation after separation by distillation. UOPs Pacol^{TM} process and UOPs Detergent Alkylate^{TM} process are examples of this approach. Huntsman Corp. (formerly Monsanto) also practices this approach [2,3].

The paraffin chlorination route followed by aluminum chloride catalyzed alkylation was used in the early 1960s. The dehydrogenation with hydrofluoric acid alkylation route became more popular in the late 1960s. It became the prominent technology because of higher-quality product and economic advantages. Additionally, the paraffin dehydrogenation routes have in general prevailed because of lower cost of the kerosene feedstock. Table 1 shows the approximate distribution of world linear alkylbenzene production using these technologies. The dehydrogenation followed by alkylation route accounts for 88% of world production.

Hydrofluoric acid is an excellent catalyst; however, potential for the accidental release of hydrofluoric acid has raised environmental safety concerns (Clean Air Act, 1990 Amendment). Maximum safety measures are taken at modern HF alkylation complexes, therefore, the potential of accidental release is minimal. Nonetheless, replacing hydrofluoric acid with a solid catalyst is desired. Recently, a new process using a

Table 1
World LAB production by technology route

Thousand metric tonnes annually	Year			
	1970	1980	1990	2000
Chlorination + alkylation	400	400	240	180
High purity olefins to alkylation	0	100	280	120
Dehydrogenation + HF alkylation	260	600	1280	1850
Dehydrogenation + solid-bed alkylation	0	0	0	260
Total	660	1100	1800	2410

solid catalyst was developed. The Detal[TM] process that uses a non-corrosive solid catalylst was commercialized in 1995.

3. Advancements in linear alkylbenzene alkylation catalysts

Hydrofluoric liquid acid was the alkylation catalyst of choice for the production of branched alkylbenzenes since 1960 when the first UOP detergent alkylation plant came on stream. The same flow scheme with minor modifications has been used for the production of linear alkylbenzenes using linear olefins derived from Pacol unit since 1968 [4]. High efficiency, superior product quality, and ease of use relative to aluminum chloride technology led to its dominance in alkylation complexes. However, the handling of corrosive hydrofluoric acid or aluminum chloride had negative implications in terms of increased capital cost for the commercial plant as well as the disposal of small amounts of neutralized waste products generated in the production process. In addition to being environmentally safe, the heterogeneous catalyst is advantageous for enabling the use of ordinary metallurgy for construction, easy separation of product and elimination of HF waste by-product.

Many acidic solids including clays, zeolites, metal oxides and sulfides have been found to be active for the alkylation of benzene with various olefins. Although many catalysts are active, they are generally lacking in selectivity to linear alkylbenzene and/or stability with respect to process time. A successful solid-bed alkylation process demands a solid acid catalyst that is active, selective, regenerable, and stable over prolonged periods of operation to be economical compared to hydrofluoric liquid acid.

Fig. 1 illustrates the reaction pathways involved in the alkylation of benzene with linear olefins. The primary product is mono-linear alkylbenzene. Dialkylbenzene is produced via consecutive alkylation. Branched olefins are produced through skeletal isomerization and react with benzene to form branched alkylbenzene. Olefins undergo oligomerization to form heavy hydrocarbons that are precursors for carbonaceous deposit on solid catalyst. The linear alkylbenzene is the only desired product. In developing a solid catalyst, controlling the formation of carbonaceous deposit is critical to making a regenerable and stable catalyst.

A description of several important discoveries in the area of solid acid catalyst development for linear alkylbenzene production follows. Because test conditions vary from laboratory to laboratory, it is difficult or impossible to rank the various materials which have been evaluated. Effects of various catalyst properties or process variables on catalyst performance will only be stressed because of this difficulty in ranking.

There have been a few studies of clays, alumina or silica–alumina supported silicotungstic acid, and aluminum silicate or magnesium silicate [5,6]. Beyond these isolated papers, not much effort has been made to study these materials because of fast deactivation and/or poor product quality.

Zeolites have been widely evaluated for the production of linear alkylbenzene [7–11]. In virtually all tests, the amount of mono-alkylbenzene is very high due to the size selectivity of the zeolites. Zeolites with relatively small channels such as H-ZSM-5 (pore size: $0.56\,nm \times 0.53\,nm$; $Si/Al = 15$) and H-ZSM-12 (one-dimensional channels: $0.62\,nm$; $Si/Al = 80$) show little activity for the production of linear alkylbenzene using 1-dodecene + benzene as the test reaction [12]. Additionally, mordenite (one-dimensional channels: $0.70\,nm$; $Si/Al = 5.5$) showed very low catalytic activity. Dealumination by steam treatment increases the activity for alkylation by opening up the mesoporosity within mordenite. Steric restrictions are still observed as a very high selectivity to 2-phenyldodecane which is the least bulky of the linear phenyldodecane isomers. Dealumination of H-Y zeolite (three-dimensional channels: $0.74\,nm$; $Si/Al = 26$) also was investigated. Non-dealuminated H-Y deactivated very rapidly with time on stream. The Al content in the framework was decreased from 50 to 10 Al per unit cell by steam heating. The effect of dealumination was to increase not only the stability of the catalyst with reaction time, but also to increase the diffusion of the molecules into and out of the zeolite pores. An almost linear relation between rate of benzene alkylation with 1-dodecene and the number of Al atoms in the framework (number of acid sites) was observed. The authors hypothesize that there is an optimum performance with the most acid sites coupled with the most open mesoporosity. The effect of acid strength was studied by using a
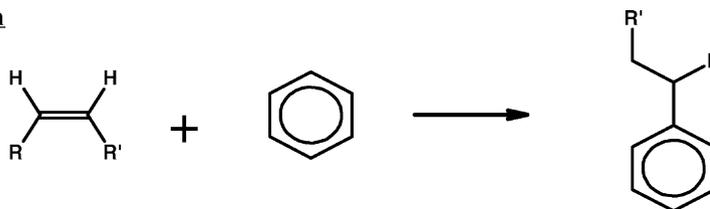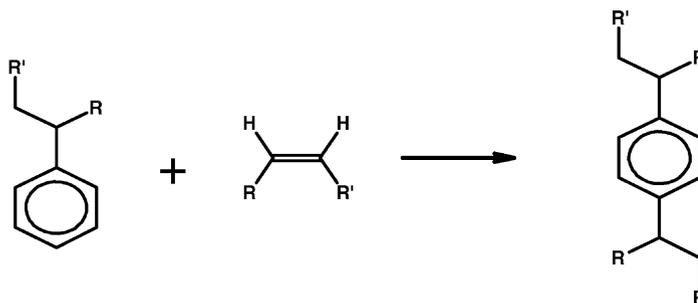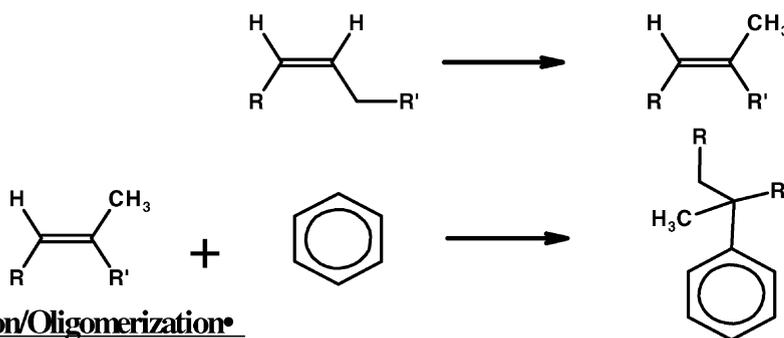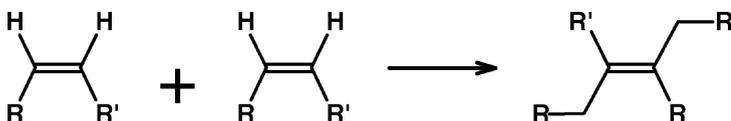
Alkylation

Dialkylation

Isomerization/Alkylation

Dimerization/Oligomerization•

Fig. 1. Key reaction in alkylation chemistry.

series of H-Na-Y zeolites for which the amount of ion exchange of Na^+ with H^+ was increased. Decreasing the sodium content in H-Y should increase not only the number of acid sites, but also the acid strength. The results for benzene alkylation with 1-dodecene clearly show a dramatic increase in turnover frequency as the percent of sodium exchanged increases

from 60 to nearly 100%. Below 60% exchange only a small effect is observed.

In another study, zeolite Beta (Si/Al = 12.5 or 25; two-dimensional 0.55 nm × 0.55 nm and 0.76 nm × 0.64 nm pore sizes) was compared to H-Y zeolite (Si/Al = 2.5 or 6; three-dimensional with 0.74 nm circular pores) and a sample of EMT

(Si/Al = 3.6; three-dimensional 0.71 nm × 0.71 nm and 0.74 nm × 0.65 nm) were evaluated under a number of conditions [13]. The Beta zeolites never achieved greater than 25% conversion of 1-dodecene. Because these materials are expected to be stronger acid catalysts, the authors felt that deactivation occurred with these samples by either acid site or pore blockage. The authors ranked activity in the order of H-Y (Si/Al = 6) > H-Y (Si/Al = 2.5) > EMT > BEA, while diffusion limitation increased as H-Y (Si/Al = 6) < H-Y (Si/Al = 2.5) < EMT < BEA. The selectivity of these materials is always skewed to the 2-phenyldodecane because of the size restrictions of the zeolite pores.

There is an interesting approach to improving catalytic stability with a solid acid catalyst. This approach involves supporting aluminum chloride on hexagonal mesoporous silica [14]. In particular, the researchers are able to produce a reusable catalyst that is prepared by chemically supporting aluminum chloride on MCM-41 type silica. The catalysts were actually prepared on hexagonal mesoporous silica supports of 1.6 or 2.4 nm pore size. In all cases, the supported $AlCl_3$ was more active per Al than tests with $AlCl_3$ as catalyst. In addition, the amount of dialkylate was less relative to $AlCl_3$ with both of the supported catalysts with less dialkylate being formed with the smaller pore catalyst. Selectivity to mono-alkylate was further improved by poisoning the external surface active sites with bulky triphenylchlorosilane or triphenylamine. Up to about 90% selectivity to phenyldodecane was observed by using this modification. The improved stability of these materials was demonstrated by decanting products from the solid catalyst after reaction and repeating the catalytic test. Catalytic activity was maintained for four tests, but only 50% conversion was achieved in the fifth cycle. No regeneration of these materials was described.

Another approach to minimizing corrosivity within a liquid alkylation system involves use of ionic liquids [15]. Ionic liquids are primarily mixtures of low melting salts such as imidazolium halides, pyridinium halides, or phosphonium halides. The active catalyst is formed by addition of $AlCl_3$ or other such Lewis acid. These are convenient catalysts systems in that the product separates cleanly from the ionic liquid, and is therefore, easily separated with the acid phase being reused. To date >99% decene conversion to

phenyldecane has been achieved with >99.5% of the ionic liquid being recyclable. Key technical hurdles in this technology include the regenerability of the ionic liquid after extended time on stream and the instability of many of these systems in the presence of water. The need to water wash alkylate product to remove trace ionic liquid or chloride must also be determined.

To date none of the above systems have been commercialized. In general, the problem has always been poor product quality and/or selectivity at economic operating conditions or insufficient long-term catalytic stability.

4. Current commercial linear alkylbenzene technology

Current technologies for linear alkylbenzene production are based on either hydrofluoric acid or a solid acid. To date, there is only one known technology using solid acid catalyst that has been demonstrated commercially. A second technology is under test in India [16]. There is little known about this technology other than it may be zeolite-based. To date, this system has not been fully demonstrated or commercialized.

The only commercialized technology is the Detal™ process offered by UOP. The Detal catalyst is a proprietary UOP solid acid developed specifically for this application [17]. This technology has two commercial units in operation to date. The flow scheme of this process is presented in Fig. 2. The process is operated in conjunction with UOPs dehydrogenation technology to produce linear olefins. The olefin feed and recycle benzene are combined with make-up benzene before introduction to the fixed-bed reactor containing the solid acid catalyst. The reaction occurs in the liquid phase under mild conditions to achieve optimal product quality. The reactor effluent flow directly to the fractionation system that is identical to that for the hydrofluoric acid process. The hydrofluoric acid stripper column, settlers, other hydrofluoric acid related piping and equipment as well as the product alumina treater are eliminated. Carbon steel metallurgy can now be used due to the elimination of the liquid acid. In order to improve product yield and quality, there are two additional components to the Detal unit. First, a DeFine™ unit to selectively hydrogenate di-olefins to mono-olefins (same as in hydrofluoric acid
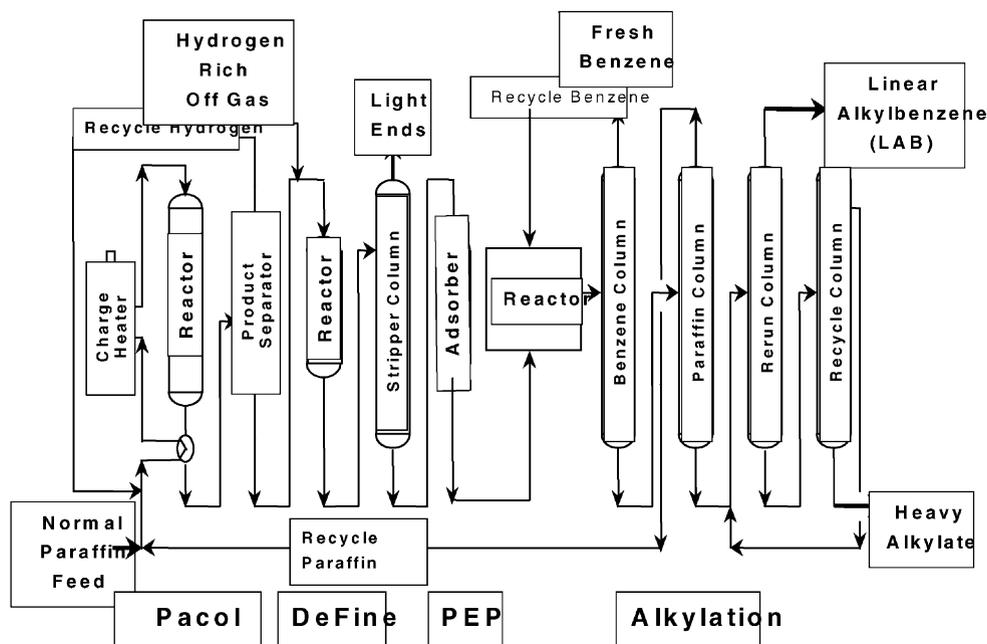
Fig. 2. Production of LAB from normal paraffin.

technology) is added to increase alkylate yield. Second, a PEP^{TM} aromatics removal unit is added to eliminate aromatics from the olefin feed stream. These aromatics would alkylate in the Detal unit leading to faster catalyst deactivation and lower quality product.

5. Product quality

Table 2 compares linear alkylbenzene product properties for the HF and Detal catalyst systems. Bromine index and sulfonatability are key measures of product

Table 2
Comparison of HF and Detal linear alkylbenzene

	HF linear alkylbenzene	Detal linear alkylbenzene
Linearity (%)	92–93	94–95
Specific gravity	0.86	0.86
Bromine index	<15	<15
Saybolt color	>30	>30
Water (ppm)	<100	<100
Tetralins (wt.%)	<1.0	<0.5
2-Phenylalkanes (wt.%)	15–18	>25
n-Alkylbenzene (wt.%)	93	95
Klett color of 5% solution	20–40	10–30

quality because they affect final product cost. High bromine index product also produced a highly colored sulfonate that required further treatment. Recently, reduction in non-alkylbenzene components, in particular reduction of tetralins and improved linearity are more important. Both of these parameters are related to improved rate of biodegradation of the ultimate product [18].

As can be seen in the Table 2, the Detal linear alkylbenzene product is produced in higher yield, with higher linearity, improved sulphonate color, and less tetralin by-product. It also has higher 2-phenylalkane content that adds improved solubility in many formulations. All of these properties demonstrate that the current Detal technology produces a superior product than the hydrofluoric acid technology.

6. Economics

Economics of the current Detal and hydrofluoric acid technology have been summarized in detail. For an 80,000 MTA linear alkylbenzene unit, the estimated erected costs for Detal and HF systems are US$ 67 and 72 million, respectively. The fixed plant

investment has been reduced by approximately 15%. The absence of the hydrofluoric liquid acid and required neutralization facilities for the acid wastes is reflected in lower operating costs.

7. Conclusions

Linear alkylbenzene is still the most cost-effective detergent intermediate. The older branched alkylbenzene technology has been nearly completely replaced by linear alkylbenzene technology. Alkylation of benzene with olefins produced by the dehydrogenation route is the technology of choice today, with solid acid catalysts emerging to slowly replace the hydrofluoric acid alkylation units. Numerous materials have been evaluated as solid acids for this alkylation process. Among the materials evaluated are zeolites, supported aluminum chloride, clays, and various metal oxides. Though significant fundamental information has been obtained on these systems, they still generally lack selectivity, catalytic stability, or successful long-term stability under commercial operating conditions. Only the UOP Detal process has been successfully demonstrated in a fully commercial unit.

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