Alkylation of Benzene with Linear Olefins over Zeotile Based Catalysts

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Declaration

This is to certify that

i) The thesis comprises my original work towards the degree of Master of Technology in Chemical Engineering (Environmental Process Design) at Nirma University and has not been submitted elsewhere for a degree.

ii) Due acknowledgement has been made in the text to all other material used.

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Abstract

Liquid phase alkylation of benzene with 1-decene as a model reaction was performed over series of zeolites catalysts, containing 30% Al_2O_3 as a binder, in a fixed bed reactor. Among the various zeolite catalysts, Zeolite-Y having SAR of 12 was found to be the most active and it showed better conversion and required 2-phenyl isomer content in the product. In the lab scale reactor, we have screened alkylation of benzene with 1-decene at various temperatures, 100-150 ^{o}C, molar feed ratios (benzene:1-decene) 5-20, zeolite SAR 9-30 and WHSV 1-2 gh^{-1} under N_2 pressure of 10 kg/cm^2, to achieve maximum olefin conversion, appropriate 2-phenyl isomer selectivity with less formation of heavier alkylates. The optimum reaction conditions of 130 ^{o}C, benzene/olefin molar ratio of 15, WHSV 1.5 gh^{-1} and time on stream 7 h, the highly active Zeolite-Y (HY-12) showed more than 85% of olefin conversion with 30% 2-phenyldecane selectivity. Based on the out come of lab scale studies, the more active and stable HY-12 was further evaluated in pilot plant using the olefin feeds having mixture of C_{10}-C_{14} (commercially used alkylation feed for LAB manufacturing). The conversion of olefin reaches almost 100% with 2-phenyl isomer selectivity of 21-23% over HY-12. The formation of heavier alkylates was observed to certain extent over the period of reaction time. Magnesium and Zinc exchanged H–Y zeolites were prepared by simple ion exchange methods with the scope of controlling heavier alkylate formation. The Magnesium exchanged HY-12 sample retain the catalytic activity as similar to HY-12 with significant improvement in reduction of heavier alkylate formation. Introduction of zinc results in lower olefin conversion with fast deactivation of catalyst.

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Nomenclature

LAB	Linear Alkyl Benzene
ABS	Alkylbenzene Sulfonate
BAS	Branched Alkylbenzene Sulfonate
HAB	Heavier Alkylbenzene
WHSV	Weight Hourly Space Velocity, gh^{-1}
BN	Bromine Number
BI	Bromine Index
DM	Double Distilled Water
V	Volume of KBr-$KBrO_3$ solution added to the sample, ml;
N	Normality of the KBr-$KBrO_3$ solution
W	Weight of sample, gm
D6R	Double Six Member Ring
XRD	X-Ray Diffraction
FTIR	Fourier Transform-Infrared
TPD	Ammonia Temperature Programmed Desorption
TGA	Thermogravimetry Analysis
SEM	Scanning Electron Microscopy
BOR	Benzene to Olefine Ratio
P	Pressure, Kg/cm^2
T	Temperature,^{o}C
HPLC	High Performance Liquid Chromatograph
GC	Gas Chromatograph
FID	Flame Ignition Detector

1. Introduction

Alkylation is the process of replacing a hydrogen atom from an organic compound with an alkyl group (C_nH_{2n+1}) [1]. The alkyl group may be transferred as an alkyl carbo-cation, a free radical, a carbanion or a carbene (or their equivalents). In petrochemical industries one of the main alkylation processes is alkylation of isobutane with olefin such as propylene, butylene) in the presence of an acid catalyst, usually sulfuric acid or hydrofluoric acid, to get high octane value stream which is blended with motor and aviation gasoline to improve the antiknock properties of the fuel. Another important process used in large scale in chemical industry is the alkylation of aromatic hydrocarbons with olefins [2]. Consider that about 75% of the 29.3 million tonnes accounting the world benzene demand in 1999, were expected to be consumed by acid catalyzed alkylation with olefins for the production of alkyl benzenes. Alkylation of benzene with linear olefins (C_{10}–C_{14}) yields linear alkylbenzenes (LAB) which is used for the manufacturing of linear alkylbenzenesulfonates, surfactants that are the main ingredient of many synthetic detergents [3-5]. LAB global demand is about 3.0 million metric tonnes per year, which is about 15% of the world consumption of synthetic detergents.

1.1 History

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. Two type of alkylate have gained industrial importance as intermediates for the production of anionic surfactant by subsequent processing to alkylarylsulfonates: (i) the branched-chain type, referred to as "hard detergent alkylate" [known after sulfonation as ABS (alkylbenzene sulfonate), BAS (branched alkylbenzene sulfonate), tetrapropylene benzene sulfonate or dodecylbenzene sulfonate], and the (ii) The "linear detergent alkylates" (or soft detergent alkylates), 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 by forming relatively stable foam streams.

In the early 1960s, the linear alkyl benzene was introduced. Due to its superior biodegradability, linear alkylbenezene sulfonates began replacing branched dodecylbenzene sulfonates. For example the propylene tetramer is still manufactured in countries that have not reached a high consumption and where accumulation in the environment has not yet been legislated. It is also used for specialized purposes such as agriculture emulsifier. “Linear alkylbenzenes” are known as LAB, and after conversion by sulfonation to “linear alkylbenznesulfonates”, they are called LAS.

The market of LAB is expected to increase faster in the developing countries as a result of the laundry bar soap and nonbiodegradable alkylbenzenes. 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. The alkylbenzene are widely used as raw material for detergent. Linear alkylbenzene now accounts for nearly all of the worldwide production of alkylbenzene sulfonates. The worldwide supply and demand of Linear Alkyl Benzene (LAB) are shown in Table 1.1 and Figure 1.1 [4, 6].

Table 1.1: Worldwide Linear Alkylbenzene Capacity/Demand in kt/year

	1987		**1992**		**1995**		**2007**	
	Capacity	Demand	Capacity	Demand	Capacity	Demand	Capacity	Demand
North America	305	287	384	337	380	520	436	415
South America	188	128	252	159	257	186	336	290
Western Europe	695	337	575	420	575	405	470	410
Asia/Pacific	490	492	709	675	968	932	1577	1472
Africa	85	52	120	92	120	115	135	125
Eastern Bloc	302	218	252	190	252	209	402	372
Total	2065	1514	2292	1873	2552	2364	3356	3084

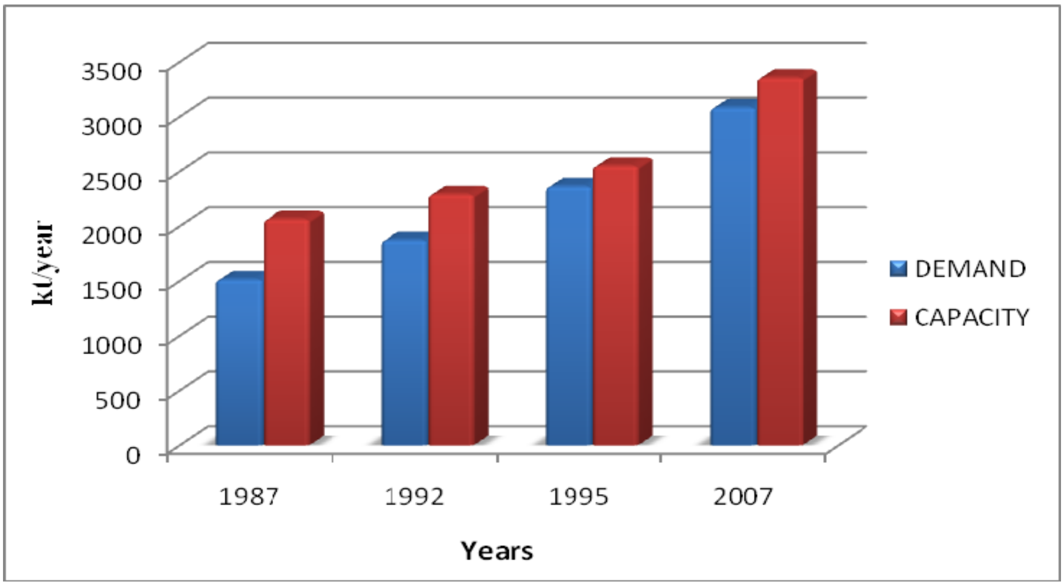


Figure 1.1 Worldwide Linear AlkylBenzne(LAB) capacity/demand; kt, kilo ton

1.2 Linear alkyl Benzene (LAB)

Linear Alkyl Benzene (LAB) is the most common raw material in the manufacture of biodegradable household detergents and surfactants. Detergents and surfactants have evolved over the years due to changes in environmental drivers, improvement in intermediate production technology, and availability of raw materials. Linear Alkyl Benzene (LAB) and Linear Alkylbenzene Sulphonate (LAS) evolved out of need for more biodegradable surfactants in the 1960's. LAB production technology has advanced significantly over nearly forty years since LAB has been produced commercially, and it continues to advance today. Sustained improvement in LAB technology have been made in the last several years that enabled producers to provide the highest quality LAB for their customers at the highest yields and the most attractive economic return. New process technology, catalysts and adsorbents have been developed and implemented providing optimal yield and quality of LAB. New innovations around established producers drove generation of new technology to meet production and cost requirement.

LAB is primarily produced from normal paraffin and benzene. LAB has commercially been produced using several different manufacturing routes. These are:

1. Dehydrogenation of n-paraffins to internal olefins followed by benzene alkylation using HF catalyst (UOP/HF n-Paraffin Process).
2. Dehydrogenation of n-paraffins to internal olefins followed by benzene alkylation using a fixed-bed catalyst (DETAL).
3. Chlorination of n-paraffins to monochloroparaffins followed by benzene alkylation with aluminium chloride ($AlCl_3$) catalyst (Friedel-Craft Alkylation).
4. Chlorination of n-paraffins to monochlorinated paraffins followed by dechlorination to produce olefins and subsequent benzene alkylation (process is however no longer commercially employed).
5. Purchased olefins reacted with benzene in the presence of HF or $AlCl_3$.

The mono-olefin is typically produced by catalytic dehydrogenation of normal paraffin. The normal paraffin is derived from straight run kerosene. The majority of LAB producers use Pacol process to produce approximately 80% of the Lab that is consumed today. LAB plant consists of the following eight process steps: (see Fig 1.2)

1. Pre-fractionation unit: Fractionation of kerosene to produce heart cut
2. Hydrobon Unit: Hydro desulphurisation and hydro de-nitrification of superior kerosene (LAB feed stock)
3. Molex Unit: Separation of n-paraffin from kerosene using Molecular sieve as an adsorbent.

4. Pacol Unit: Conversion of n-paraffin to olefins.
5. DeFine Unit: Selective dehydrogenation of di-olefins to mono-olefins
6. Pep unit: To eliminate aromatics from the olefin feed stream.
7. Alkylation Unit: Alkylation of olefins and benzene in presence of HF catalyst of LAB.
8. Neutralization Unit: Acidic vapours are neutralized with circulating KOH in scrubber.

Linear alkylbenzenes (LAB) with long-chains (typically 10–14 carbon) are commonly used commercial products which have some conceivable positional isomers, i.e. 2-, 3-, 4-, 5-, 6-phenyl, etc. A high percentage of 2 phenyl isomer is desired because it has the highest biodegradability, solubility and detergent properties among the related isomers. Typically, the alkylated aromatics are manufactured commercially using Friedel-Crafts alkylation of benzene with HF. Such methods produce high conversions, but the selectivity to 2-phenyl isomers is only about 20%, and selectivity is also low with highly heavier aromatics, so selectively catalyzed alkylation is desired widely in the world.

In addition, these acidic catalysts in commercial processes are extremely corrosive in nature, thus requiring special handling and equipment metallurgy. Furthermore, the use of these acids might also induce some environment problems. With increasing environmental concern, it is more and more important to find substitutes equal or superior to these acid catalysts in all respects. Therefore, it would be desirable to utilize a safer and simpler catalyst, preferentially in heterogeneous medium, to produce the desired products.

Most of current heterogeneous processes of alkylation, disproportionation, and transalkylation of aromatics involve the use of zeolites based catalysts. Since zeolites are having, uniform pore size, high surface area and which helps to get high selectivity of products, in environmentally safe conditions. They are a widely studied class of materials with tremendous advantages to replace anhydrous HF or $AlCl_3$ catalyst. In addition, due to their narrow pore dimensions, the selectivity to 2-phenyl isomer is higher than that of HF catalyst. Many kinds of zeolites have been studied in recent years, but they are easily deactivated and it is difficult to industrialize them. Figure 1.3 shows the different alternative routes to produce Linear Alkylbenzene.

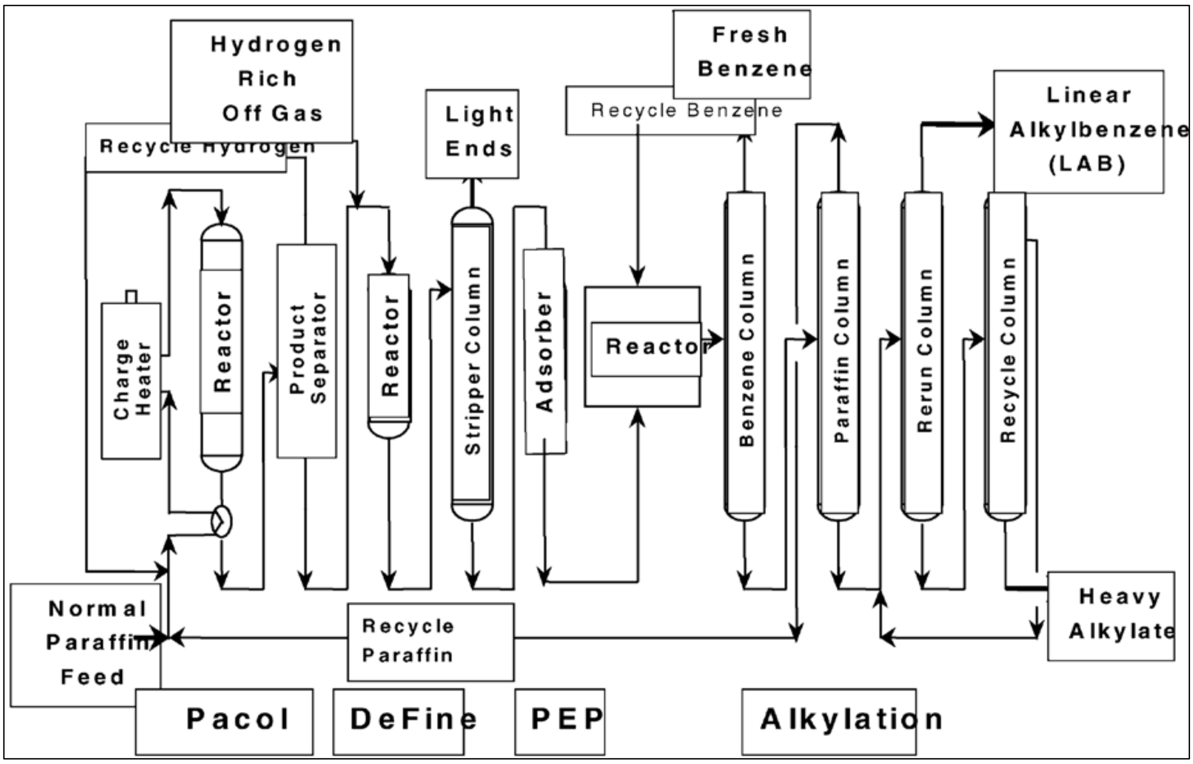


Figure 1.2 Production of LAB from normal paraffin with DeFine process[7].

1.3 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 kerosene 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 zeolite has dominated as the adsorbent of choice. Commercial process technologies for absorption process include UOP^{TM} Molex^{TM} process, UOP^{TM} IsoSiv^{TM} (formerly Union Carbide) process, Exxon Ensorb process and the GDR Parex process [7].

(1) About 80% of linear alkylbenzenes manufactured in the world are produced via UOP technology with the use of Pacol Process: dehydrogenation of a relatively cheap fraction of n-C_{10}-C_{13} paraffins and hydrogen fluoride alkylation of benzene with the dehydrogenation products containing olefin with internal double bonds.

(2) In addition, about 11% of the world productions of linear alkylbenzenes are manufactured via the alkylation of benzene with n-paraffin dehydrogenation products in the Detal process on heterogeneous catalysts.[8-11]

(3) The linear paraffins are obtained in >98% purity by fractionation recovery processes. These linear paraffins are converted into alkyl chlorides or olefins, and alkylating benzene with them produces linear alkyl benzenes. The above processes are also adapted by various technologies such as:

(a) Chlorination of linear paraffins to form monochloroparaffin. Aluminum chloride catalyst is used to alkylate benzene with the mono-chloroparaffin. For example, ARCO Technology Inc. [12] has developed and commercialized this route.

(b) 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.

(c) 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.

(d) 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 [13, 14].

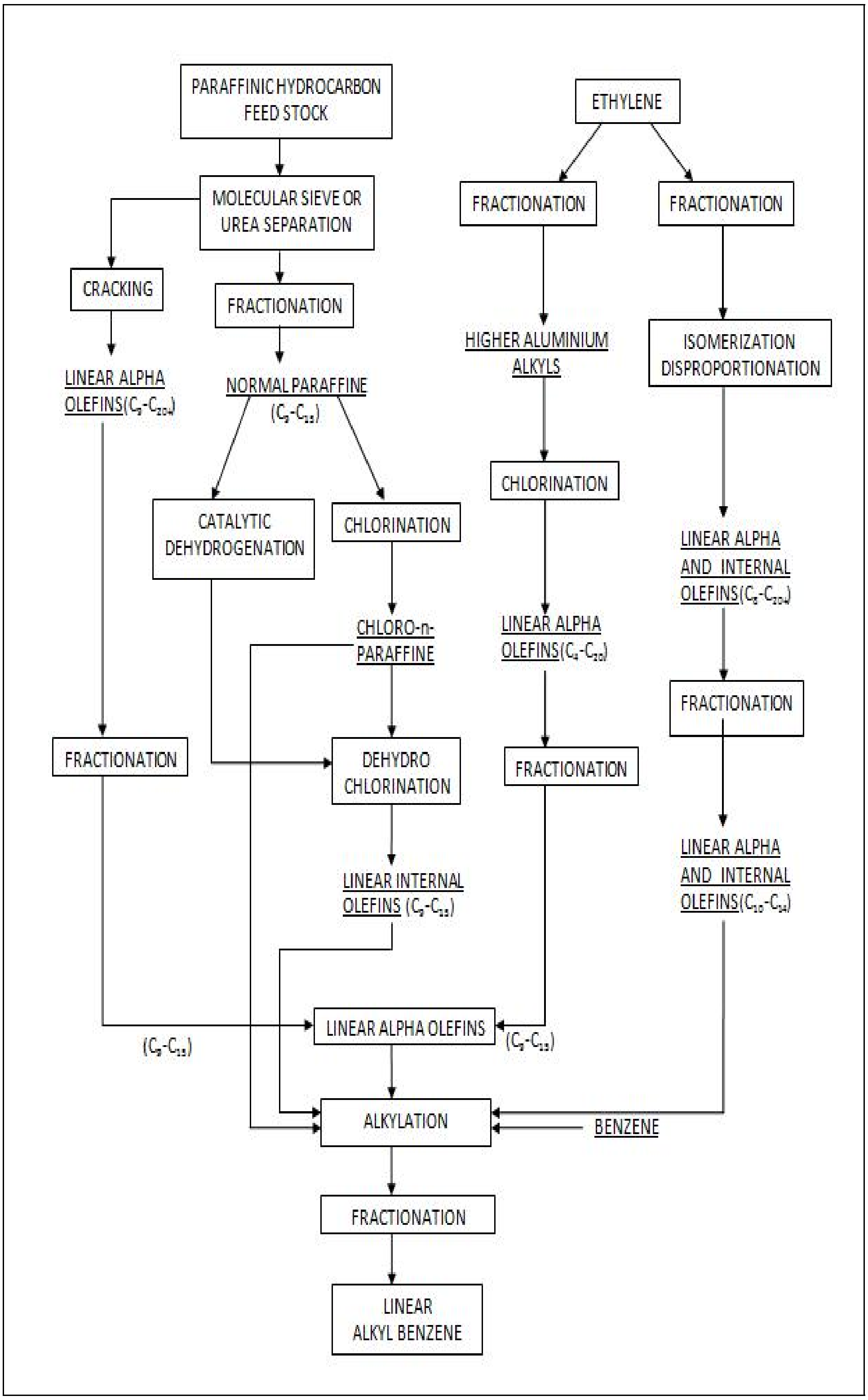


Figure 1.3 Alternative routes to Linear Alkylbenzene.

The paraffin chlorination route followed by aluminium 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 1.2 shows the approximate distribution of world linear alkylbenzene production using these technologies.

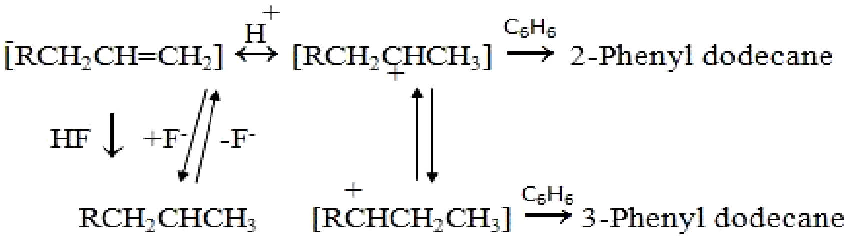
The dehydrogenation followed by alkylation route accounts for 88% of world production. Hydrofluoric acid is an excellent catalyst; however, potential for the accidental release of hydrofluoric acid has raised environmental safety concerns (Clean Air Act, 1990 Amendment). Maximum safety measures are taken at modern HF alkylation complexes, therefore, the potential of accidental release is minimal. Nevertheless, replacing hydrofluoric acid with a solid catalyst is desired. Recently, a new process using a solid catalyst was developed. The Detal^{TM} process that uses a non-corrosive solid catalyst was commercialized in 1995.

Table 1.2: World LAB production by technology route

	Year				
Thousand metric tonnes annually	**1970**	**1980**	**1990**	**2000**	**2010***
Chlorination + alkylation	400	400	240	180	100
High purity olefins to alkylation	00	00	280	120	50
Dehydrogenation + HF alkylation	260	600	1280	1850	1500
Dehydrogenation + solid-bed alkylation	0	0	0	260	1200
Total	660	1100	1800	2410	2950

1.4 The Chemistry of Alkylation for LAB Formation

The generally accepted mechanism for alkylation of arenes with alkenes involves interaction of the alkene with the acid catalyst to from an alkylcarbenium ion, a corresponding ion pair or polarized complex (15). The alkylcarbonium ion undergoes a rapid secondary rearrangement in varying degree, followed by attack on the nucleus of the arenes in a rate-determining step to from the product (16-18). This mechanism can be represented, as shown in scheme 1, when HF (Hydrofluoric acid) is used as a catalyst.



Scheme 1. Reaction Mechanism of Alkylbenzen Production

Side reaction also can take place: such as Dimerization of the olefin, alkylation of this dimer, dialkylation of benzene, possible diphenylation of the olefin or chloroparaffin and cyclo-alkylation of the benzene (19). Thus, during the reaction, in addition to formation of the LAB, some by product will be found. These include diphenyl alkane, and dialkylbenzene, or 1,3-dialkylindanes and 1,4-dialkyltetralins. These heavy by-products are separated from LAB by distillation, and they are called “heavy alkylate”. However it is some times difficult to separate dialkylindanes, dialkyltetraline and branched alkybenzene from LAB because they have almost the same molecular weight.

The heavy alkylate from chloroparaffins is similar to that from the olefin-based product and is sulfonated either by oleum or SO_3 to produce synthetic petroleum sulfonates. The heavy alkylate can only be partially sulfonated because here, sulfonation take place almost invarisbly in the para-position, and when it is blocked, no sulfonation occurs. The heavy alkylate normally contains 60-70% of sulfonated matter. The sodium salts of heavy alkylated sulfonates are used as emulsifiers, wetting agent and dry cleaning additives. The alkyline earth salts (Ca, Ba and Mg) are used in lubricants and greases, and their “over-based” varieties (adding surplus hydroxide or carbonate to neutralize in such a way that the base remains in colloidal suspension) are used as rust preventatives (19, 20).

Secondary-to-secondary rearrangement of the alkylating agent occurs with linear alkenes, resulting in the formation of isomeric alkylcarbenium ions, which after reaction with benzene, yield isomeric phenylalkanes. There are three major catalysts for the industrial production of LAB: $AlCl_3$, HF and Zeolites. These three catalysts gives different phenyl isomer distribution in LAB produced. The $AlCl_3$ catalyst gives what is called the high 2-phenyl product: 30% 2-phenyl isomer, 20% 3-phenyl isomer, and gradually decreasing amounts (to 15-16%) of the 5- and 6- phenyl isomer.

Table 1.3: Typical composition (wt %) of Commercial Linear Alkylbenzene Products[a]

Product components	**Catalyst**								
	HF	$AlCl_3$	$AlCl_3$	HF	$AlCl_3$	HF	$AlCl_3$	HF	$AlCl_3$
	Alkylating Agent								
	a	b	a	a	-	a	-	b	a
n-Alkyl benzene	93	88	98	99.5	83.8	92.2	82.9	-	-
2-Phenyl Alkanes	18	29	29	29	30	-	-	17	28.8
Dialkyltatraline	0.5	9	0.5	0.46	16.2	0.45	13.9	0.1	11.7
Branched Alkylate	-	-	-	-	-	7.04	1.83	2.5	1.2
Heavy Alkylate	-	-	-	-	-	0.13	-	0.3	-
Molecular Wt.	240	241	240	242	240	242	241	241	244

[a] Alkylating agent; a = n-Olefin; b = Chloroparaffin; HF = Hydrofluoric acid.

With the HF catalyst, these are a flatter distribution, with all phenyl isomer present at about the same level, approximate between 17-20%. This LAB is called low 2-phenyl product. Almost two third of LAB comes from the HF process. Most of the alkylate in the liquid products is probably from $AlCl_3$ process; the situation is just the reverse in powder product. The typical composition of commercial LAB is presented in Table 1.3 [4]. The differences in composition markedly affect formulating properties of LAS in liquid detergents, particularly solubility and viscosity.

2. Literature Survey

2.1 Current Status in 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 [21]. 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^{TM} process offered by UOP. The Detal catalyst is a proprietary UOP solid acid developed specifically for this application [22]. This technology has few commercial units in operation to date. 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 flows 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^{TM} unit to selectively hydrogenate di-olefins to mono-olefins (same as in hydrofluoric acid 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. Recently research interest on LAB is to use zeolites based catalyst.

2.2 Introduction to Zeolites

The history of zeolite began in 1756 when the Swedish mineralogist Cronstedt discovered the first Zeolite mineral, stildite [23]. He called the mineral a zeolite derived from the two Greek words, “Zeo” and “lithos” meaning “to boil” and “a stone”. Zeolites are highly crystalline, porous, hydrated aluminosilicates of natural or synthetic origin with a three-dimensional framework of SiO_4 and AlO_4 tetrahedra, each of which contains a silicon or aluminum atom in the center. The oxygen atoms are shared between adjoining tetrahedra. Zeolites may be represented by the formula:

$$M^{n+}_{1/n} \,.\, AlO_2 \,.\, xSiO_2 \,.\, yH_2O$$

Where,

M = counter ion
n = counter ion valency
x = silicon / aluminum ratio
y = content of hydrate water

The Lowenstein rule allows only the formation of zeolites having Si/Al >=1. The counter ion is often a metal cation. The counter ions neutralize the negative charge of the framework, as seen in Figure 2.1.

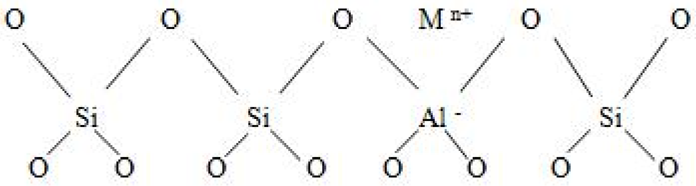


Figure 2.1 Part of a Zeolite structure.

Natural zeolites form where volcanic rocks and ash layers react with alkaline ground water. Zeolites also crystallized in post-depositional environments over periods ranging from thousands to millions of years in shallow marine basins. Naturally occurring zeolites are rarely pure and are contaminated to varying degrees by other minerals, metals, quartz or other zeolites. For this reason, naturally occurring zeolites are excluded from many important commercial applications where uniformity and purity are essential.

More than 150 zeolite types have been synthesized and 48 naturally occurring zeolites are known. But among 48 types of natural zeolites of interest to catalysis, only a few are found in abundance and even fewer have found industrial use. The industrial applications of zeolite catalysts depend largely on our ability to synthesize zeolite, and the synthesis of known and new structures has made new discoveries in zeolite catalysis possible. Zeolites have an “open” structure that can accommodate a wide variety of cations, such as Na^+, K^+, Ca^{2+}, Mg^{2+} and others. These positive ions are rather loosely held and can readily be exchanged for others in a contact solution. An example mineral formula is: $Na_2Al_2Si_3O_{10}$-$2H_2O$, the formula for natrolite.

Zeolites are the aluminosilicate members of the family of microporous solids known as “molecular sieves”. The term molecular sieve refers to a particular property of these materials, i.e. the ability to selectively sort molecules based primarily on a size exclusion process. This is due to a very regular pore structure of molecular dimensions. The maximum size of the molecular or ionic species that can enter the pores of a zeolite is controlled by the diameters of the tunnels. These are conventionally defined by the ring size of the aperture, where, for example, the term “8ring” refers to a closed loop that is built from 8 tetrahedrally coordinated silicon (or aluminium) atoms and 8 oxygen atoms. These rings are not always perfectly flat and symmetrical due to a variety of effects, including strain induced by the bonding between units that are needed to produce the overall structure, or coordination of some of the oxygen atoms of the rings to cations within the structure. Therefore, the pore openings for all rings of one size are not identical.

Zeolites have a uniform pore structure determined by the crystal structure with known pore diameters (channels) between 3 and 10 Ǻ. The channels may be circular or elliptical, tubular or containing periodic cavities and straight or zigzag. If the counter ions are located within a channel they can be exchanged and hence the catalytic capacity of zeolite may be enhanced. Apertures consisting of the ring of oxygen atom of connecting tetrahedral limit access to the channel. There may be 4, 5, 6, 8, 10 or 12 oxygen atoms in the ring. The regular structure of pores and with their aperture in the atomic scale enables the zeolite to work as a molecule sieve and hence zeolite can have high selectivity’s as catalyst for certain reactions. The pore size and structure of zeolites may affect the selectivity of a reaction in one or more of three ways [24]. Figure 2.2 represent the different type of shape selectivity of zeolite catalyst.

1. ***Reactant selectivity:*** The pore size can hinder certain reactant from reaching the interior of the zeolite. This occurs when the apertures from smaller then the molecules i.e. only sufficiently small molecules can the active sites. Hence the term “molecular sieve” is justified. An example where reactant selectivity is important is in reforming processes of high-octane gasoline [25].

2. ***Product selectivity:*** Products larger then the aperture size can not diffuse out from the zeolite. Therefore these larger molecules will not be formed or they will be converted to smaller molecules or to carbonaceous deposits within the pore. Unfortunately this may deactivate the zeolite due to pore blockage. An example of a reaction where product selectivity is important is the Alkylation of toluene over H-ZSM-5 [13].

3. ***Restricted transition state selectivity:*** This third of shape selectivity causes less undesirable side reactions or hinders larger intermediates that would be formed in other environments, to escape from the pore. Only those intermediates that can fit in the pore can be formed. However, in practice it is difficult to distinguish restricted transition state selectivity from product selectivity. An example of a reaction where restricted transition state selectivity is important is the methanol-to-gasoline process (MTG) which uses an H-ZSM-5 catalyst.

2.3 Uses of Zeolites

2.3.1 Commercial and Domestic

Zeolites are widely used as ion-exchange beds in domestic and commercial water purification, softening, and other applications. In chemistry, zeolites are used to separate molecules (only molecules of certain sizes and shapes can pass through), as traps for molecules so they can be analyzed.

Zeolites have the potential of providing precise and specific separation of gases including the removal of H_2O, CO_2 and SO_2 from low-grade natural gas streams. Other separations include: noble gases, N_2, O_2, Freon and formaldehyde. However at present, the true potential to improve the handling of such gases in this manner remains unknown [26].

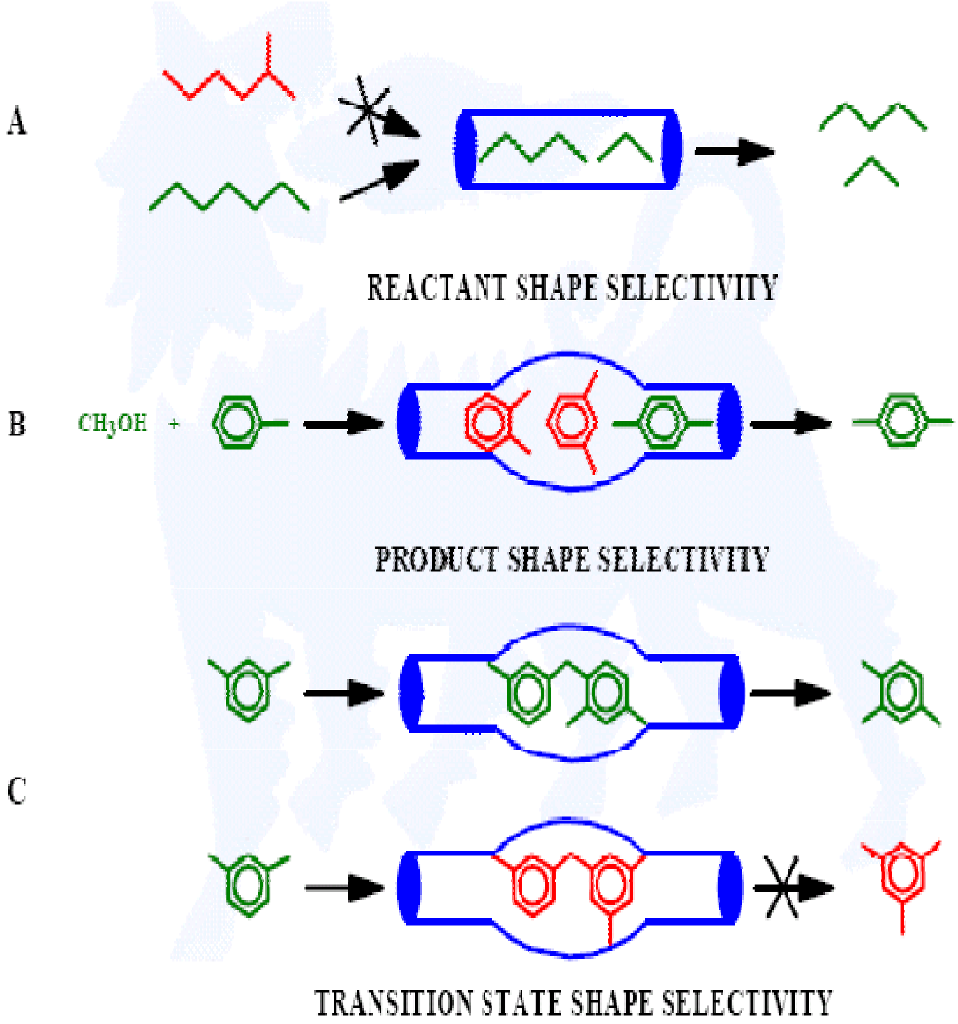


Figure 2.2 Different shape selectivity of zeolite catalyst [27].

2.3.2 Petrochemical industry

Synthetic zeolites are widely used as catalysts in the petrochemical industry, for instance in fluid catalytic cracking and hydro-cracking. Zeolites confine molecules in small spaces, which cause changes in their structure and reactivity. The hydrogen form of zeolites (prepared by ion-exchange) is powerful solid-state acids, and can facilitate a host of acid-catalyzed reactions, such as isomerisation, alkylation, and cracking. The specific activation modality of most zeolitic catalysts used in petrochemical applications involves quantum-chemical Lewis acid site reactions. Catalytic cracking uses a furnace and reactor. First crude oil distillation fractions are heated in the furnace and passed to the reactor. In the reactor the crude meets with a catalyst such as zeolite. It goes through this step three times, each time getting cooler. Finally it reaches a step known as separator. The separator collects recycled hydrogen. Then it goes through a fractionator and becomes the final item.

2.3.3 Nuclear Industry

Zeolites have uses in advanced reprocessing methods, where their micro-porous ability to capture some ions while allowing others to pass freely allow many fission products to be efficiently removed from nuclear waste and permanently trapped. Equally important are the mineral properties of zeolites. Their alumino-silicate construction is extremely durable and resistant to radiation even in porous form. Additionally, once they are loaded with trapped fission products, the zeolite-waste combination can be hot pressed into an extremely durable ceramic form, closing the pores and trapping the waste in a solid stone block. This is a waste form factor that greatly reduces its hazard compared to conventional reprocessing systems [26].

2.3.4 Agriculture

In agriculture, clinoptilolite (a naturally occurring zeolite) is used as a soil treatment. It provides a source of slowly released potassium. If previously loaded with ammonium, the zeolite can serve a similar function in the slow release of nitrogen. Zeolites can also act as water moderators, in which they will absorb up to 55% of their weight in water and slowly release it under plant demand. This property can prevent root rot and moderate drought cycles.

2.3.5 Animal Welfare

In Concentrated Animal Growing facilities, the addition of as little as 1% of a very low sodium clinoptiloite was shown to improve feed conversion, reduce airborne ammonia up to 80%, act as a mycotoxin binder and improve bone density. It can be used in general odor elimination for all animal odors.

2.3.6 Medical

Zeolite-based oxygen concentrator systems are widely used to produce medical grade oxygen. The zeolite is used as a molecular sieve to create purified oxygen from air using its ability to trap impurities, in a process involving the absorption of undesired gases and other atmospheric components, leaving highly purified oxygen and up to 5% argon. Zeolite was once the active component in QuikClot, a hemostatic agent used as an emergency coagulant in the veterinary industry before being found to be toxic.

2.3.7 Heating and Refrigeration

Zeolites can be used as solar thermal collectors and for adsorption refrigeration. In these applications, their high heat of adsorption and ability to hydrate and dehydrate while maintaining structural stability is exploited. This hygroscopic property coupled with an inherent endothermic (heat absorbing) reaction when transitioning from a dehydrated to a hydrated form, make natural zeolites useful in harvesting waste heat and solar heat energy.

2.3.8 Detergents

The largest single use for zeolite is the global laundry detergent market. This amounted to 1.44 million metric tons per year of anhydrous Zeolite-A in 1992.

2.3.9 Construction

Synthetic zeolite is also being used as an additive in the production process of warm mix asphalt concrete. The development of this application started in Europe (Germany) in the 1990s. It helps by decreasing the temperature level during manufacture and laying of asphalt concrete, resulting in lower consumption of fossil fuels, thus releasing less carbon dioxide, aerosols and vapours. Other than that the usage of synthetic zeolite in hot mixed asphalt leads to easier compaction and to a certain degree allows cold weather paving and longer hauls .When added to Portland cement as a Pozzolan, it can reduce chloride permeability and improve workability. It reduces weight and helps moderate water content while allowing for slower drying which improves break strength.

2.3.10 Gemstones

Thomsonites, one of the rarer zeolite minerals, have been collected as gemstones from a series of lava flows along Lake Superior in Minnesota and to a lesser degree in Michigan, U.S.A.. Thomsonite nodules from these areas have eroded from basalt lava flows and are collected on beaches and by scuba divers in Lake Superior.

These thomsonite nodules have concentric rings in combinations of colors, black, white, orange, pink, red and many shades of green. Some nodules have copper as inclusions and rarely will be found with copper "eyes". When polished by a lapidary the thomsonites sometimes display chatoyancy.

2.3.11 Aquarium Keeping

Zeolites are marketed by pet stores for use as a filter additive in aquariums. In aquariums, zeolites can be used to absorb ammonia and other nitrogenous compounds. However, due to the high affinity of some zeolites for calcium, they may be less effective in hard water and may deplete calcium. Zeolite filtration is used in some marine aquaria to keep nutrient concentrations low for the benefit of corals adapted to nutrient-depleted waters.

Where and how the zeolite was formed is an important consideration for aquariums. Northern hemisphere natural zeolites were formed when molten lava came in contact with sea water, thereby 'loading' the zeolite with Na (sodium) sacrificial ions. These sodium ions will speciate with other ions in solution, thus the takeup of nitrogen in ammonia, with the release of the sodium. In southern hemisphere zeolites, such as found in Australia, which were formed with fresh water, thus the calcium uptake on formation? Zeolite is an effective ammonia filter, but must be used with some care, especially with delicate tropical corals which are sensitive to water chemistry and temperature.

2.3.12 Space Hardware Testing

Zeolites can be used as a molecular sieve in cryosorption pumps for rough pumping of vacuum chambers which can be used to simulate space-like conditions in order to test hardware bound for space.

2.4 Characteristics Properties of Zeolites

- Crystalline and therefore precisely defined arrangement of SiO_4 and AlO_4 tetrahedra. This result in good reproducibility in production.
- Shape selectivity only molecules that are smaller than the pore diameter of the zeolite undergo reaction.
- Controlled incorporation of acid center in the intra-crystalline surface is possible during synthesis and/or by subsequent ion exchanger.
- Above 300^oC pentasil and zeolite Y have acidities comparable to those of mineral acids.

- Catalytically active metal ions can be uniformly applied to the catalyst by ion exchange or impregnation. Subsequent reduction to the metal is also possible.
- Zeolite catalysts are thermally stable up to 600^oC and can be regenerated by combustion of carbon deposit. They are well suited for carrying out reaction above 150^oC, which is of particular interest for reaction whose thermodynamically equilibrium lies on the product side at high temperature.[24]

2.5 Heterogeneous Catalysts for Benzene Alkylation with Olefins

Most of the current zeolites based processes of alkylation, disproportionation, and transalkylation of aromatic hydrocarbons involve the use of supported acid catalytic complexes or solid acid catalysts. The application of liquid superacid catalytic complexes, for example, on the basis of Group II–III metal chlorides or Group V–VI metal fluorides, is fraught with their tendency to catalyze the unwanted reactions of the isomerisation and disproportionation of alkanes and the degradation and polymerization of olefins, thus creating stirring, catalyst isolation, and spent-catalyst regeneration problems and causing corrosion of the equipment [28]. At the same time, liquid acids are active in alkylation of benzene at temperatures below 100°C and supported acids are active at temperatures up to 200°C, whereas aluminosilicate catalytic systems are usually effective at higher temperatures, thereby requiring the application of high pressures [28–38].

The possibility of benzene alkylation on activated clay [39] or synthetic aluminosilicates [40] was established as early as the 1940s. To substitute for insufficiently active and thermally stable ion-exchange resins used at 120–140°C in phenol alkylation with C_9-C_{12} olefins [32, 35–37], in particular, in alkylation by propylene tetramers, montmorillonite activated by inorganic acids (H_2SO_4, HCl,HNO_3, or a mixture of hydrochloric and phosphoric acids) was suggested [41]. Catalysts of this type exhibit activity in alkylation with octene-1 and decene-1 at temperatures of about 170°C.

Alkylation of benzene with higher olefins C_7-C_{10} was also performed in the presence of heterogeneous catalysts with deposited Nb(**V**) and Ta(**V**) halides [42,43]. Alumina-supported Ti chlorides and fluorides [44],Sn, Pb, and Mg compounds [45], and Mo trioxide

[46] were also used. The application of silicotungstic acidsupported on silica gel or aluminosilicate to alkylationof benzene with C_{11}-C_{14} olefins was reported by Aboul Cheit et al. [47]. They showed that the activity of the silicotungstic catalyst based on aluminosilicate depends not only on the specific surface area, but also on the SiO_2:Al_2O_3 molar ratio and the rate of this reaction is relatively low, despite its low activation energy (12-13 kJ mol^{-1}), because it is limited by internal diffusion of the reactants.

In patents [48–50], aluminosilicate hydrates with the zeolite or clay structure, in particular, kaolinite and smectite, as well as macroporous X and Y zeolites and mordenite, modified with Al, Cr, Fe, Co, Ni, and Cu ions and treated with various acids were used as catalysts for benzene alkylation with the products of the dehydrogenation of C_{10}-C_{14} paraffins. According to Tejero et al. [48], the catalyst can ensure an olefin conversion higher than 90% with a selectivity of 80–85% (for linear alkylbenzenes).

A catalyst for benzene alkylation with C_{10}-C_{14} olefins based on the Filtrol-13 clay modified by the addition of 20% alumina and Group IIIA, IIIB, and IVB metals was patented by UOP [51]. In particular, a catalyst based on this clay modified by cerium nitrate (3 wt % Ce) and air-steamed at 600°C was tested in the benzene alkylation reaction at 150°C under a pressure of 3.5 MPa. The conversion of C_{10}-C_{14} olefins reached 99% with a yield of the alkylation products of 91.35% (with 95% linear alkylbenzenes).

Brazilian bentonite of the smektite type was also used as a support of the catalyst for benzene alkylation with 1-dodecene [52]. To modify the distance between clay layers in the preparation of so-called pillared clays, bentonite was treated with solutions of aluminium salts. To obtain intercalate (interlayer phase), a mixture of aluminum chloride with alkali was used. After treatment with a solution at an OH/Al molar ratio of 2 at 60°C (pH 4) and calcination at 500°C , the catalyst wastested. Feedstock at a benzene/olefin molar ratio of 215 was fed with the mass rate olefin/catalyst = 1 for 6 h. The maximum conversion of 1-dodecene was about 50%. It is obvious that the activity of this catalyst is relatively low, probably, because of the low acidity of the active sites.

The possibility of attaining a very high acidity of crystalline aluminosilicates stimulated studies of zeolites catalysts as catalysts for benzene alkylation not only with ethylene or propylene (to obtain ethylbenzene and cumene), but also with higher olefins. For propylene, the conversion and acidity of the catalysts decreased in the order MgY > CaY > SrY > BaY.

The activity of acid catalysts based on zeolites depends on the silica modulus (SiO_2/Al_2O_3 ratio), the extent of the replacement of alkaline cations with polyvalent cations or protons, the presence of acid promoters, and the size of windows and channels in their crystal lattice [28, 31, 36, 38]. Using Zeolites based benzene alkylation catalysts, it is necessary to take into account steric hindrances for the alkylation reaction, especially for higher olefins. Olefins with a higher molecular mass are characterized by a higher reactivity and selectivity.

In alkylation of benzene with a fraction of C_{10}-C_{18} α-olefins at a molar ratio of up to 100 : 1 at 180°C and a feed space velocity of 0.25 h–1 on zeolite Y modified by rare-earth elements, the yield of monoalkylbenzene reached 86–92% of the theoretical value. Together with 2-phenylalkanes, which are preferred due to their biodegradability, other isomers were also formed [38]. In particular, alkylation of benzene at 180°C and 1 MPa on lanthanide-promoted zeolite Y made it possible to obtain about 94% undecylbenzene [33]; the conversion of benzene increased from 31 to 69% upon alkylation with dodecene at 220°C on high-silica pentasil-type zeolites with an increase in the Si/Al molar ratio from 17.8 to 38.5. A conversion of about 67% was also attained on macroporous mordenite with a lower Si/Al ratio (6.5) [53].

Wang et al. [54] reported the results of studies of modified zeolite Y samples in the linear alkylation of benzene with 1-dodecene (at a molar ratio of 1:4). The tests were performed under a nitrogen pressure of 1.0 MPa and a contact time with the feedstock of 3 h; the best results were obtained on highly dealuminated (SiO_2/Al_2O_3= 80) zeolite USH-Y at 180°C : the olefin conversion was 97.8% with the selectivity for linear alkylbenzenes of 99%. Most publications on testing zeolite catalysts in the alkylation reactions with higher olefins lack data on the possibility of a long reaction cycle.

In the patent literature, many high-silica zeolites (X, Y, L, and β), in particular, with Al_2O_3 as a binder, are recommended for the alkylation of arenes with C_2-C_{20} olefins at 120–400°C. Zeolite-containing catalysts for benzene alkylation with ethylene, propylene, and higher linear olefins are also proposed by Süd-Chemie [28]. In the patent of the Huntsman Petrochemical Corporation [55], to prepare a catalyst for benzene alkylation with higher olefins, mordenite with a silica ratio of 17 was used, whose acidity was increased by the introduction of fluorine (up to 4%). The alkylation of benzene with the products of the dehydrogenation of C_{10}-C_{14} paraffins was conducted at 75–200°C and relatively low space velocities (0.2–0.4 h^{-1}).

In spite of the industrial application of the catalyst DA-112 and, later, the new modification DA-114, in the Detal process, information on their characteristics has not been published. This Detal process, having undeniable ecological advantages over hydrogen fluoride alkylation, has insignificant technical advantages over the former process with the use of adsorption dearomatization of the dehydrogenation products of higher paraffins (PEP). However, both charges of the alkylation catalyst loaded to alternately switched reactors and the catalyst consumption are relatively high in this case as well.

Although zeolite catalysts possess relatively high acidity and activity, the development of more efficient systems and processes for the manufacture of linear alkyl benzenes on the basis of zeolites presents some problems due to the microporous structure of the catalysts and, hence, diffusion hindrances to both the alkylation and desorption of heavy by products during "regeneration" by solvents. In the last 10–15 years, information has been published on the creation of super acid heterogeneous catalytic systems, whose acidity is higher than that of zeolites catalysts [56–59]. Among these are, in particular, heteropolyacids of the type $H_3PW_{12}O_{40}$ or a cesium salt of this acid $Cs_x H_{3-x} PW_{12}O_{40}$, where $x = 1, 2, 2.5$, or 3, which, according to the published data [37], can mediate butane isomerization in the absence of traces of alkenes. The low-temperature isomerization of *n*-butane is used to estimate the strength of acid sites of solid superacids as a test for their activity in other reactions.

Wide possibilities for varying the acid properties and pore characteristics of superacid catalytic systems based on metal oxides, in particular, high-silica zeolites and similar mesoporous materials, and zirconium oxide promoted by sulfate ions, suggest that the design of new active and selective catalysts of this type holds promise for the development of the corresponding processes for the manufacture of linear alkylbenzenes.

2.6 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 [60]. 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 aluminium 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 having superior activity, selectivity, re-generable, and stable over prolonged periods of operation and importantly it should be economical compared to hydrofluoric liquid acid. The primary product of alkylation of benzene is mono-linear alkylbenzene. Di-alkylbenzene is produced via consecutive alkylation. Branched olefins are produced through skeletal isomerisation 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 heterogeneous catalysts 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 aluminium silicate or magnesium silicate [23, 61]. 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 [62–64]. In virtually all tests, the amount of mono-alkylbenzene is very high due to the size selectivity of the zeolites. Zeolites with relatively narrow channels such as H-ZSM-5 (pore size: 0.56 nm × 0.53 nm; Si/Al = 15) and H-ZSM-12 (one-dimensional channels: 0.62 nm; Si/Al = 80) show considerable activity for the production of linear alkylbenzene for the test reaction using 1-dodecene as alkylating agent [65]. The large pore Mordenite (one-dimensional channels: 0.70 nm; Si/Al = 5.5) also showed relatively very low catalytic activity. Dealumination by steam treatment increases the activity for alkylation by opening up the mesoporosity within Mordenite. Steric restrictions was observed over zeolite catalysts, and results very high selectivity to 2-phenyldodecane, since it 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 helps on increase the diffusion of the molecules within 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 effect of acid strength was studied by using large pore zeolites (Si/Al = 3.6; three-dimensional 0.71 nm × 0.71 nm and 0.74 nm × 0.65 nm) were evaluated in several reaction conditions [66]. The Beta zeolites never achieved greater than 25% conversion of 1-dodecene. Because these materials are known that have stronger acid catalysts, where the deactivation occurred with these samples by either acid site or pore blockage.

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 aluminium chloride on hexagonal mesoporous silica [67]. In particular, the researchers are able to produce a reusable catalyst that is prepared by chemically supporting aluminium 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.

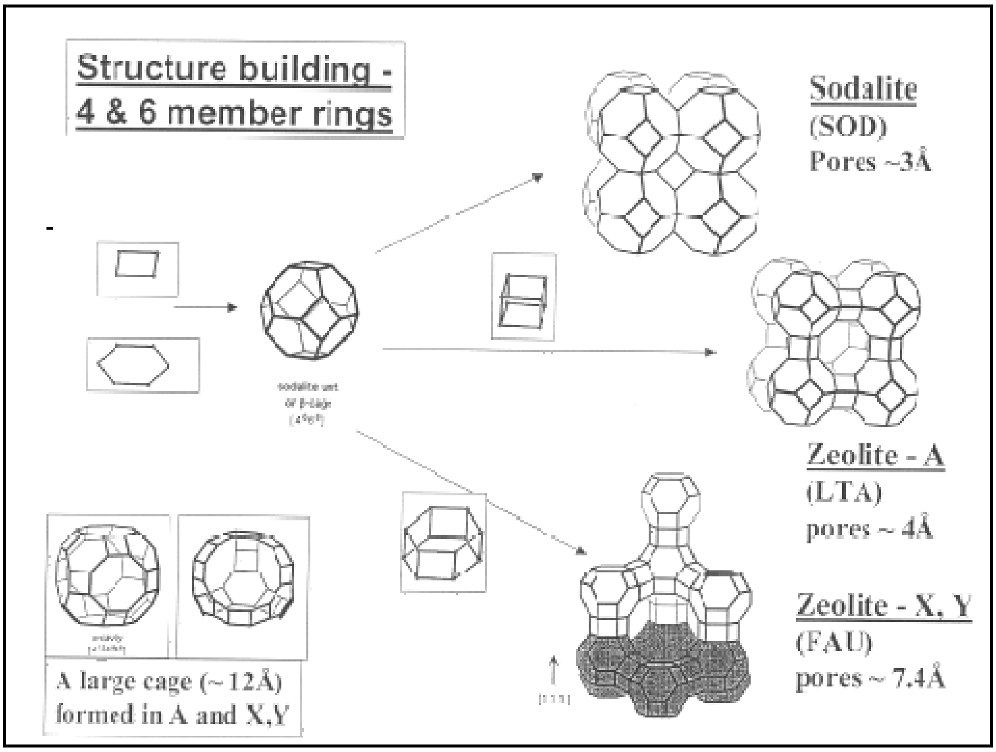
Selectivity to mono-alkylate was further improved by poisoning the external surface active sites with bulky triphenylchlorosilane or triphenylamine. Up to about 90% selectivity to phenyldodecane was observed by using this modification. The improved stability of these materials was demonstrated by decanting products from the solid catalyst after reaction and repeating the catalytic test. No regeneration of these materials was described.

Another approach to minimizing corrosivity within a liquid alkylation system involves use of ionic liquids [68]. 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.

As is already known in the detergent industry, linear alkylbenzene sulfonates (LAS) with high 2-phenyl (20-30 %) and low tetralin content (heterogeneous processes) is easier to formulate into liquid detergents than that with a lower content in those components (HF process with 15-20% 2-phenyl). While the 2-phenyl content significantly affects the solubility, tetralins have a marked depressive effect on viscosity. A high quality of LAS is produced by the heterogeneous process with olefins. In heterogeneous process zeolites has shows good potential to produce high 2-phenyl especially with large pore zeolites like Mordenite, MCM and zeolites-Y. A high quality of LAS with better solubility in water will be found the high market value. Finally, LAS produced by the DETAL process already in the market and a other technologis is under test and will commercialised in some years. It will give these two products component at high 2-phenyl content and low tetralin content. The conclusion is that, in spite of 2-phenyl being the less soluble isomer, in commercial LAS, solubility increases with an increase in 2-phenyl content.

2.7 Large Pore Zeolites

Zeolites of interest to shape selective catalysis may be divided into three major groups according to their pore/channel system. These are 8-membered Oxygen Ring System, 10-membered Oxygen Ring System, and 12-membered Oxygen Ring System. Recently, it is also known zeolites having both 8 and 12-membered oxygen ring and 10 and 12-membered oxygen ring (MCM-22) combination. Zeolites with 12-membered Oxygen Ring openings, such as faujasite, are generally known as large pore zeolites. Zeolite Y comes under this category. The pore opening of this type of zeolite is around 0.74 nm. Application of this type of zeolites has wide range such as paraffin hydroisomerization and hydrocracking, catalytic cracking, the liquid alkylation of benzene with olefins and the isomerization alkylaromatics. Figure 2.3 shows the structure and 3-D view of large pore Zeolite (Y type) catalyst.



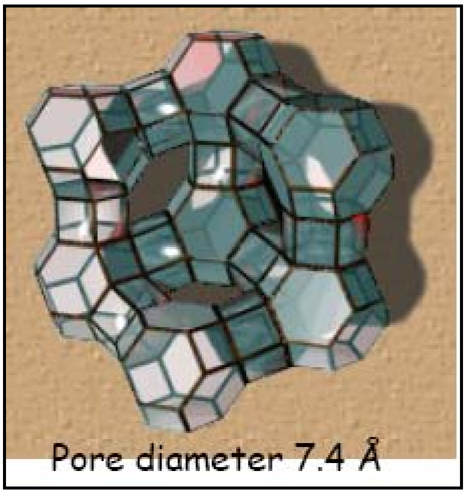


Figure 2.3 Structure and 3-D view of large pore zeolite (Y type) catalyst

2.8 Aim and Scope of Work:

Our aim of the present work is to understand the various zeolites behaviour on alkylation of benzene with 1-decene as a model reaction for the LAB processes and also scale up the superior catalysts in to the pilot plant level:

- Study the effect/dependence of the various operating parameters. Such as feed ratio, pressure, temperature, WHSV, gas flow etc on the catalytic activity.
- Estimating the parameters and optimum reaction condition and conversion for given set of process condition.
- Identify the factors determining the product distribution, 2 phenyl isomer, linearity, formation of heavier aromatics etc.
- Effect of various modifications of zeolites on heavier aromatics formation (for example, zinc and Magnesium modified zeolites).
- Develop process more environmentally friendly and more profitable.
- Gain better insight into the behaviour of Zeolite catalyst.

2.9 Objective of Project

Objective of our project to develop environment friendly zeolite based solid acid catalysts for LAB processes, which can provide best quality of linear alkyl benzene in better operating and process condition and also reduce the capital and processing cost. The following technical parameters have been analysed in details to achieve better quality of LAB by using zeolites catalysts, which are:

1. Reduce the formation of Heavier aromatics
2. Get desirable rage of 2-phenyl isomer
3. Increase yield and linearity
4. Higher activity and selectivity

3. Experimental Work

Alkylation of benzene with 1-decene is chosen as a model reaction for the linear alkyl benzene (LAB) synthesis. A series of zeolite samples such as Zeolite-Y, Mordenite, Zeolite-β, MCM-22 have been selected for screening for catalyzing the above reaction under standard procedure known from literature [64]. Among them, the highly active catalyst will be studied at different reaction parameters (temperature, space velocity (WHSV), molar ratios) in details, both in lab and pilot plant scale to achieve maximum olefin conversion, with appropriate 2-phenyl content selectivity with less heavy alkylate formation. Table 3.1 summarized the textural properties of various zeolites chosen for the model reaction.

Table 3.1: Chemical and physical properties of zeolites used for alkylation reaction

Source of Sample	**Zeolites catalyst**	**SiO_2/Al_2O_3, Molar Ration**	**Surface Area, m^2/g**
In house prepared	HY-9 (300)*	9	445.6
	HY-9 (200)*	9	782
	HY-9 (170)*	9	638
CBV-712	HY-12	12	730
CBV-720	HY-30	30	780
CBV 21A	MORDENITE	20	500
CP 814E	H-β	25	680
In house prepared	MCM-22	30	404
CBV-760	HY-60	60	720

*Number in the bracket shows the particle size of particular sample

3.1. Synthesis of Zeolite –Y with SAR of 9 and Different Particle Sizes

We attempted synthesis of large pore zeolite-Y with the aim of using it as catalyst for LAB process. Following chemicals were used in the syntheses of zeolite-Y.

- Colloidal silica HS-40 (40 wt.% of Silica)
- Sodium aluminate anhydrous
- Sodium hydroxide pellets
- Cetyltrimethylammonium bromide (CTMABr)
- Double distilled water
- Ethyl alcohol

The gel composition used for this synthesis of the nano sized zeolites Y was: 9 SiO_2: $1Al_2O_3$: (0-0.018) CTMABr: $3Na_2O$: 120 H_2O. In a typical synthesis, 17.6311 g of sodium hydroxide and 25.124 g of sodium aluminates was dissolved in 99.2 g of double distilled water. To this solution about 175.6 g of colloidal silica was added and the resulting mixture was stirred until the homogeneous aluminosilicates gel formed. The resultant gel was aged at room temperature for 22 h. In the case of sample synthesized in presence of surfactant; before aging process at RT, CTAMBr was slowly added in to the homogeneous aluminosilicate gel and stirred vigorously and then final gel was aged at RT for 22h.

After aging for 22 hours at RT, the sample was aged at 90^0C for 2 hours. Then the mother liquor was substituted by an equal amount of 1.55M sodium hydroxide solution. The batch was then aged at 90^0C for 1-3 days. Further, sample also synthesized using different CTABr concentration to get different particle size of zeolite-Y. The final products were washed with distilled water and dried either for 24 hours at 90^0C. In order to remove the surfactant, the as-synthesized samples were calcined in a temperature programmed (Indotherm) tubular furnace under flowing air, (60 - 100 ml min^{-1}). The heating was carried out from room temperature to 550 ^oC with a controlled heating rate of 1^oC min^{-1} for 6 h.

In order to maintain the electrical neutrality of the zeolite (Zeolite-Y; aluminosilicate) network, exchangeable cation like in the present studies sodium was introduced during the synthesis of these materials. When these exchangeable cations were replaced by protons the material exhibits Brӧnsted acidity. The acid form of Zeolite-Y was prepared from the Na^+ form of Zeolite-Y as per the procedure described below. First, NH_4^+ form of Zeolite-Y was obtained by repeated ion exchange of Na. form of AlMCM-41 with 1 M NH_4NO_3 at 353

K for 6 h. The protonated form of the catalyst, i.e. H-Y, was obtained by calcination of NH_4^+ form of the catalyst at 550 ^oC for 6 h.

3.2. Characterization

Several analytical and spectroscopic techniques were employed to characterize all the synthesized (Zeolite-Y) samples. The details are given below.

3.2.1. X-ray Diffraction (XRD)

Powder XRD patterns were recorded on a D8 ADVANCE diffractometer (Brucker axs). The patterns recorded for all the synthesized samples in order to verify the formation and nature of structure. The diffraction patterns were recorded in the 2θ range of $5\text{–}50^0$ using X-ray diffractometers, equipped with nickel filtered Cu K_α radiation (λ = 1.5418Å). The scan speed and step size was 0.5^o min^{-1} and 0.02^o respectively.

3.2.2. Fourier Transform-Infrared (FT-IR) Spectroscopy

FT-IR spectra of the various samples were recorded on a by Nicolet 6700 (Thermo Scientific) with a 4 cm^{-1} resolution and 128 scans in the mid IR (400 - 4000 cm^{-1}) region using KBr pellet technique. About 10 mg of dry KBr was mixed with a little amount (one hundredth of the KBr amount) of the sample and ground for homogenization under IR lamp. It was then pressed into a transparent, thin pellet at 5 tons cm^{-2}. These pellets were used for IR spectral measurements.

3.2.3. Ammonia Temperature Programmed Desorption (NH_3-TPD)

The acidic behavior of the protonated catalyst was studied by temperature programmed desorption of ammonia (NH_3-TPDA) with Chemisorb 2750 (Micro Metrix). About 50-100 mg of protonated acid catalysts was placed in quartz reactor and was activated at 400 ^oC in air for 6 h followed by 2 h in helium with a flow rate of 50 ml min^{-1}. Then the reactor was cooled to 100 ^oC and maintained for another hour under the same condition. Ammonia adsorption was carried out by injecting the gas (500 μl) through the sample for several times at this temperature. Subsequently, it was purged with helium for an hour to remove the physisorbed ammonia. The desorption of ammonia was carried out by heating the reactor up to 600 ^oC at a rate of 10 ^oC min^{-1} using a temperature programmer. The amount of ammonia desorbed was estimated with the aid of thermal conducting detector (TCD) response factor for ammonia.

3.2.4. Scanning Electron Microscopy (SEM)

SEM was used for observation of the crystal size distribution of the studied particles. A thin focused beam of electron with energy of 10 to 50 keV is directed to the surface. The intensity of the secondary electrons by the primary beams was measured by a detector. As the primary beam starts to move (to scan) above the sample the secondary electron signal, as a function of momentary spot of the electron beam, becomes visible. Thus a three dimensional object of high resolution could be visible due to the output of secondary electrons. During the contact of the electron beam with the sample a characteristic X-ray radiation is produced. The element specific energy of the secondary radiation is used for qualitative analysis of the sample by Energy Dispersive X-ray Analysis (EDXA/EDAX).

3.2.5. Thermogravimetry Analysis (TGA)

Thermogravimetry (TGA) analysis measurements were carried out on a Shimazdu DT-30 TG and DTA system in nitrogen /air atmosphere (40 ml min^{-1}) with 12–15 mg of the sample with a heating rate of 10 ^{o}C min^{-1} in the temperature range of 300–1073 K. A simultaneous TG-DTA (Dupont 9900/2100) was also used for this purpose.

3.3 Preparation of Extrude

All catalysts were in the powder form. In order to get better strength and proper shape we made extrude of catalysts. Extrude mixture was prepared by using 70:30 wt/wt ratios of zeolite and binder. ‘Condia’ Alumina was used as binder. Acetic acid (27.3 vol %) was used to mix binder and zeolites.

A solution of 27.3 vol. % acetic acid was prepared from glacial acetic acid with appropriate dilution using deionised water. The calculated amount of catalyst (zeolites) and binder ‘Condia’ alumina powder was first mixed properly. Then acetic acid solution was added in small amount and pegged thoroughly to get hard gel. Hard gel was pressed through sodium pressing machine to get extrude. The finally extrude were dried at room temperature for 1-2 hr followed by 110 ^{o}C for overnight and calcined at 540 ^{o}C for 6 hr in a tubular furnace in a air atmosphere.

3.4 Preparation of Metal Exchanged Zeolites

To modify the acidity of Zeolite catalyst the proton sites were ion-exchanged with divalent metal ions such as Zinc and Magnesium. Zinc nitrate and Magnesium acetate was used as source of Zn and Mg. About 0.01 wt. % metal solution was prepared in 250ml standard volumetric flask. About 50 g of zeolite was taken in to a round bottom flask containing 250ml of metal salt solution and ion-exchange was carried out by continuous refluxing for 24 h. After refluxing 24 hr the zeolite sample was washed with distilled water for 4-5 times, then dried and calcined it at 540^{o}C for 6 hr.

3.5 Reaction Procedure

Initial studies carried out in lab scale reactor by choosing model reaction. Benzene and 1-decene was two main component of our reaction system. For better reaction and good contacting between benzene and olefin it is essential that benzene remains in liquid state. To maintain homogeneous phase we kept pressure constant at 0.6 MPa. Literature shows that near this pressure benzene will remains in liquid state, thus during whole study the pressure was kept constant. For initial screening studies, we kept the pressure (0.6 MPa), temperature (100 ^{o}C) and WHSV (1.5 gh^{-1}) constant. The above conditions were found to be ideal for heterogeneous catalysis for the linear alkyl benzene synthesis, since such conditions the catalytic deactivation was known to be minimal. The lower deactivation noted at 0.6 MPa is probably due to the solvent action of liquid benzene dissolving away the deactivating components from the catalyst surface. In a typical run, the feed mixture was prepared by mixing of known amount of benzene mixed appropriate concentration of 1-decene present in decane solution. The decane was used as diluents. Table 3.2 gives the composition of feed for different molar ratio.

After evaluation of series of catalysts at lab scale, the superior catalysts studied in pilot plant using long chain paraffin having about 12 % long chain (C_{10}-C_{14}) mono olefin. The composition of feed was analyzed by HPLC. (Paraffins = 82.365wt%, Di-olefine = 0.102wt%, Aromatics = 5.389 wt%).

Table 3.2 Composition of feed with different molar ratio

Feed Ratio	**Benzene**	**1-Decene**	**Decane**
5	55.4	20	133.8
10	110.8	20	133.8
15	166.2	20	133.8
20	221.8	20	133.8

3.6 Reactor Setup

Evaluation of catalyst was carried out in fixed bed, continuous flow, electrically heated Stainless steal small scale reactor system with 5 gm catalyst charge. For pilot plant reaction set up 30 gm catalyst was used. The schematic diagram of the same is given below. The reactor is configured to have the reactant and carrier gas flowing in the upward direction. The feed from feed tank is pumped at appropriate rate to the through an adsorbent column containing molecular sieve in order to remove feed moisture below 20 ppm.

The moisture depleted feed enter the reactor mixed with carrier gas through the bottom and flow upwards. Beds of inert glass beads (2 mm) were placed both upstream and downstream catalyst bed. The inert at upstream were used both for positioning the catalyst bed in the isothermal zone of the furnace and as well as for feed preheating while those at catalyst bed downstream were used to weigh down the catalyst and prevent its carryover from the reactor. The feed comes in contact with catalyst bed in the rector and effluent stream exit the reactor from the top. The temperature of catalyst bed is constantly monitored through a central thermocouple located within the catalyst bed.

The reactor effluent stream passes through an air condenser and a gas-liquid separator and collects in the product tank. Sample is drawn from this at appropriate interval. After draining the product completely, small sample is drawn for analysis. The vent gas stream from the gas-liquid separator passes through a fine control mechanical manual metering valve (used for throttling vent gas flow rate and thus controlling system back pressure) and is diverted to vent at safe height. Sufficient pressure is maintained in the reactor so as to keep benzene, one of the liquid reactants in the liquid state at reaction temperature.

2.7 Product Analysis

Feed analysis: a typical feed was prepared by mixing appropriate quantities of Benzene and alky feed (or synthetic mixture of n-paraffin & mono olefin) in order to achieve the required Benzene to Olefin ratio. Fresh alky feed was obtained from LAB Plant BC from PACOL stripper which is at downstream location of DEFINE reactor. The Bromine Number of the feed was determined by titration method. The feed was not stored for more than a week prior to use.

Bromine Number **(BN)** is the number of grams of bromine consumed by 100 gram of the sample when reacted under the specified condition.

Bromine Index **(BI)** is the number of miligrams of bromine consumed by 100 gram of the sample when reacted under the specified condition. By the definition “bromine index” is equal to 1000 times the “bromine number”

In other words, the bromine Number, which gives a measure of unsaturation (mono and di olefins), is expressed as the number of grams of bromine consumed by 100 gm of the sample when reacted under standard condition (65).

3.8 Reagents Needed for Bromine Number

- Carbon Tetrachloride
- Acetic Acid-glacial
- Sodium thiosulphate solution (approximately 0.1 N accurately standardized) Dissolve 25.9 of $Na_2S_2O_3.H_2O$ in water and add 0.01 gm of Na_2CO_3 to stabilize the solution. Dilute to 1 liter and mix thoroughly by shaking.
- Potassium Iodide Solution 150 gm per liter
- Potassium Bromide-Bromate solution (standard 0.5 N) weigh out exactly 51.0 gm of potassium bromide and 13.92 gm of potassium bromated, dissolve in distilled water, and dilute the solution to 1 liter.

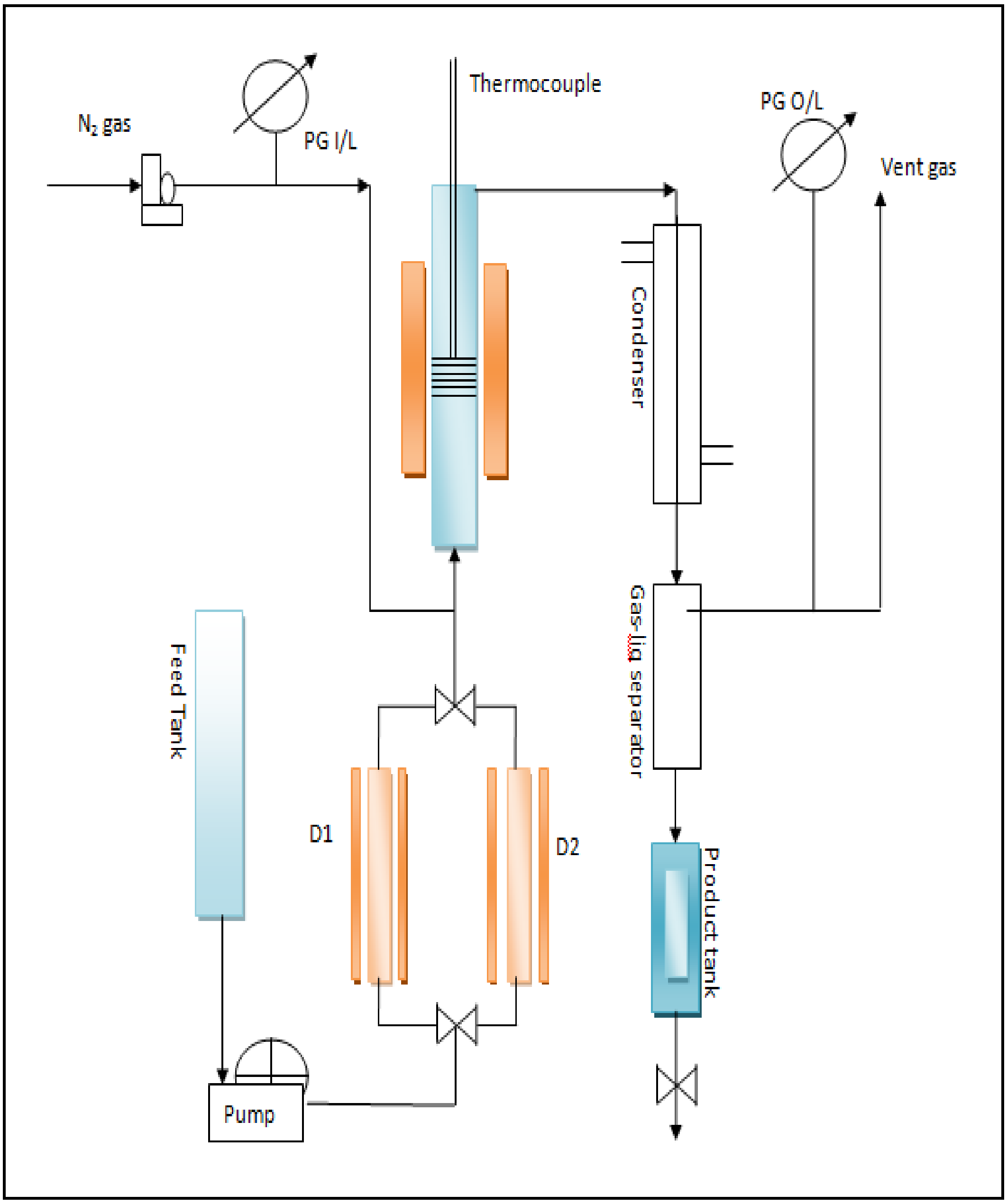


Figure 3.1 Schematic flow diagram of reactor set-up

In addition to the above reagents, the following titrating mixture is also needed; every liter of the BNS solution must constitute:

• Glacial Acetic Acid (AR Grade)	1428 ml
• Carbon Tetrachloride (AR Grade)	268 ml
• Methanol (AR Grade)	268 ml
• 1:5 Sulfuric Acid (AR Grade)	36 ml

Normality of $Na_2S_2O_3$ = (0.1 x 25) / Burette reading

3.9 Standardization Procedures

3.9.1 Standardization of Sodium Thiosulphate Solution

In a clean dry beaker, weigh out 0.1226 gm of pure $K_2Cr_2O_7$ and dissolve in 50 ml DM water. In a flask, weigh out 3.0 gm of Potassium Iodide (KI) and 2.0 gm $NaHCO_3$. Add 100 ml distilled water and 6 ml conc. Hydrochloric acid to the flask. Carefully add the contents of the beaker to the flask. Rinse the beaker with 50 ml DM water. Keep the flask in the dark for 10 minutes.

3.9.2 Standardization of KBr-$KBrO_3$ Solution

Take 50 ml Acetic acid and 1 ml conc. Hydrochloric acid in an iodine flask, stopper it and put in ice bath for 10 minutes. Then add 5 ml KBr-$KBrO_3$ solution to it drop wise. Stopper it cool in ice bath for another 5 minutes and put 5 ml KI in lip of flask. Let it stand for 5 minutes in ice bath and shake vigorously for 1 min, add KI and appox. 100 ml DM water. Titrate it with the standardized $Na_2S_2O_3$ solution. Color will change reddish brown to yellowish here add 2 ml starch indicator color will change to colorless and it will be end point.

Normality of KBr-$KBrO_3$ = Reading * Normality of $Na_2S_2O_3$ / 5

This is an amperometric titration. The Pt-Pt electrode directly measures the current in the olefin in the solution and current baseline remains steady as long as the Br species are consumed by the olefin sample. When the latter no longer takes up any more of Br, the current in the solution shoots up, indicating the completion of titration.

Method: Accurate weight out 0.6 – 0.8 gm of the sample. Add 70 ml of BNS to it. Titrate it with the standardized KBr-$KBrO_3$ solution from the burette.

Bromine Number = 7.99 * (NV) / W

Where,

V = Volume of KBr-$KBrO_3$ solution added to the sample, ml;

N = Normality of the KBr-$KBrO_3$ solution;

W = Weight of sample, gm

3.10 Product Characterization

The liquid product collected from the reservoir was subjected to Bromine Index estimation using an Auto titrator and amperometric titrating method with double point electrode. The sample was solubilized with a solvent containing of glacial acetic acid, CCl_4, methanol, conc. H_2SO_4 and mercuric chloride. In order to estimate the HAB content accurately, the product sample was subjected to ambient pressure distillation to remove unreacted Benzene prior to GC analysis. Since the atmospheric distillation residue tends to become yellow in color indicative of thermal degradation, one sample was subjected to vacuum distillation. However no significant change was realized in the result.

The residue containing paraffin, trace un-reacted olefins, LABs (Linear Alkyl Benzene) and HABs (Heavy Alkyl Benzene) was then analyzed by capillary gas chromatography using FID. Gas chromatographic analysis of this sample allows determination of selectivity to 2-phenyl isomer content in LAB, linearity and HA/Alkylate weight ratio. The data from all this analyses was collected to get material balance and performance parameters. It was not possible to determine the chemical identity of the components under the category HAB.

Performance criteria-Definition:

Olefin conversion (wt %): 100*(grams/hr Olefin in feed – gram/hr olefin in product) / (grams/hr olefin in feed)
= 100*(BI of feed – BI of product) / (BI of feed)
Where BI (Bromine Index): 1000*grams of Bromine consumed by 100gm sample

3.11 Characterization of in-house Prepared Zeolites-Y Catalysts

Figure 3.2 illustrates the FTIR pattern for zeolite-Y catalysts prepared in house. All the samples showed typical vibration bands around 1600 cm^{-1} characteristic of aluminosilicate framework. In addition there are three weak bands around 577cm^{-1}, 614 cm^{-1} and 433 cm^{-1} due to as-symmetric and symmetric vibration of T-O-T, where T= Si or Al, which are arise from secondary building unit (D6R). The above observation evidences the formation of zeolite-Y framework.

The X-ray diffraction pattern was employed for further characterization of the studied zeolites during crystallization. Figure 3.3 shows the XRD pattern of all in house synthesized samples. All the samples showed a pure Y-zeolite phase with high crystallinity. The pattern and intensity of the XRD of all the samples tells the standard characteristics of zeolite-Y nature. The XRD peak broadening occurs on the sample synthesized in presence of surfactant indicates that the particle size might be relatively smaller.

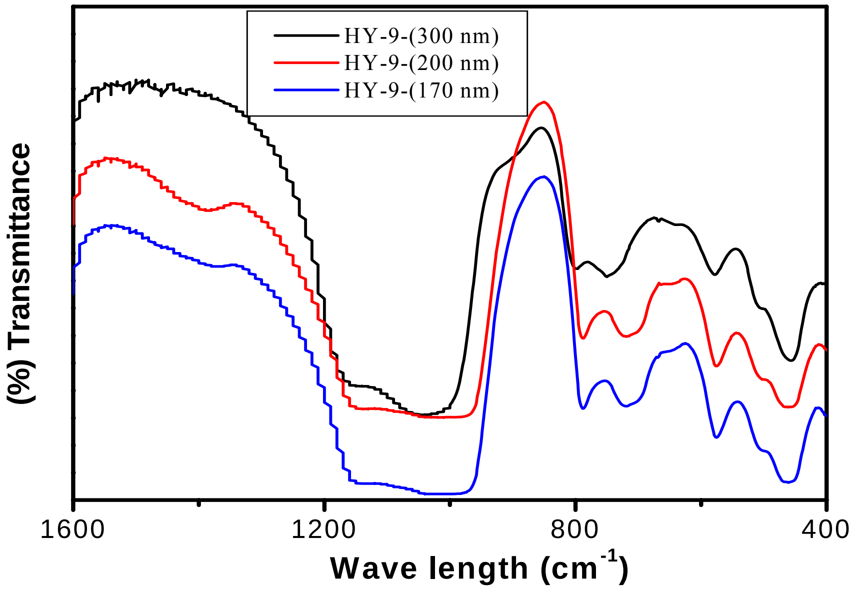


Figure 3.2 IR spectra of the zeolites-Y synthesized with different particle size.

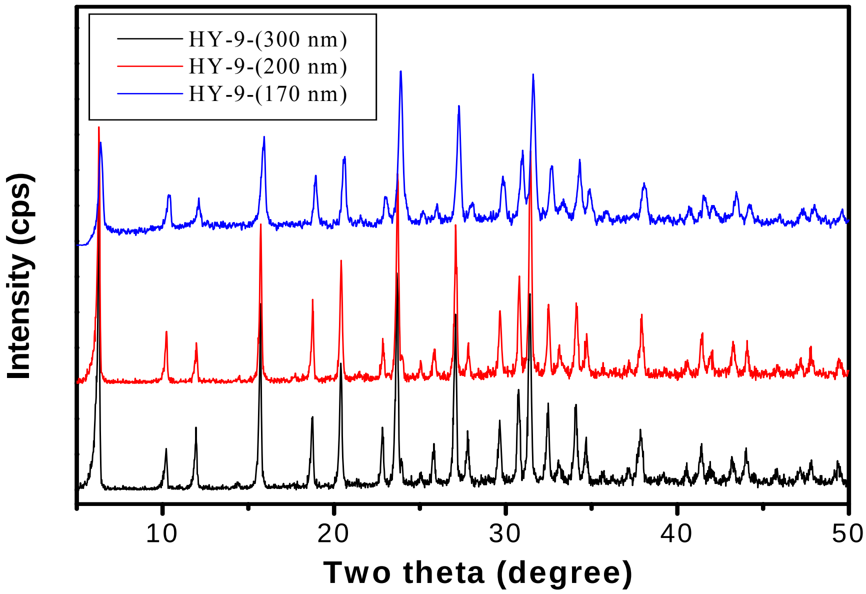


Figure 3.3 X-ray diffraction patterns of zeolite samples prepared in house

Figure 3.4 to 3.6 show the SEM images of zeolite-Y synthesized at different conditions. All the samples showed uniform spherical particle size in the range of 300-150 nm ranges. The sample synthesized in presence of surfactant showed relatively smaller particle size HY-9(170) compared to sample synthesized in absence of surfactant HY-9(300) and HY-9(200). The sample synthesized by 3 days crystallization leads to small particle size HY-9(200) than sample synthesized at short time (1 day) showed HY-9(300), which is due to dissolution of uncondensed silica in alkaline solution and high crystallization in long period.

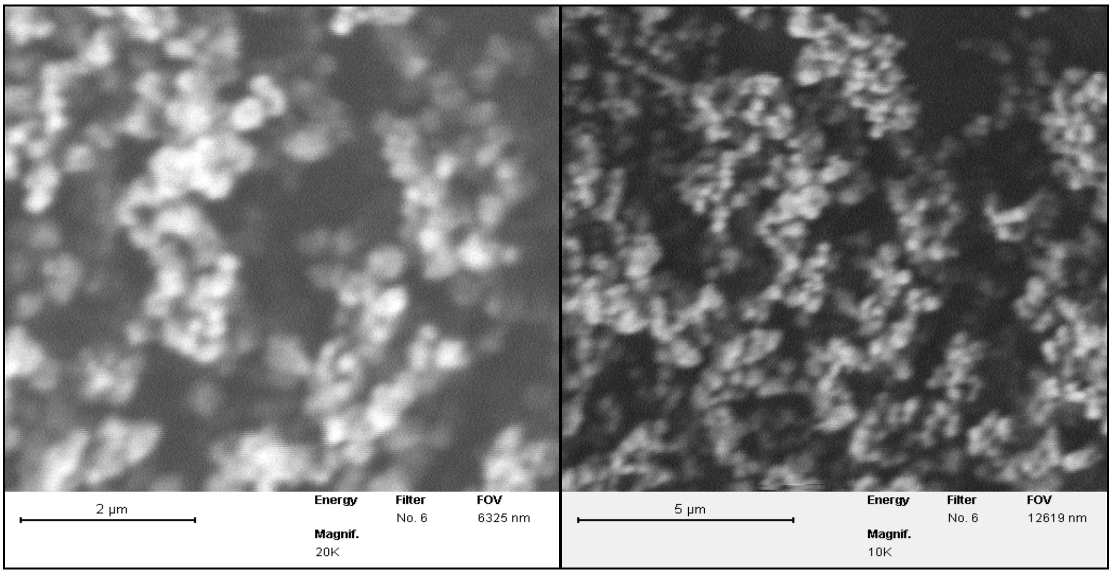


Figure 3.4 SEM images of HY-9(300) after 1 day aging, particles of 200 nm are produced

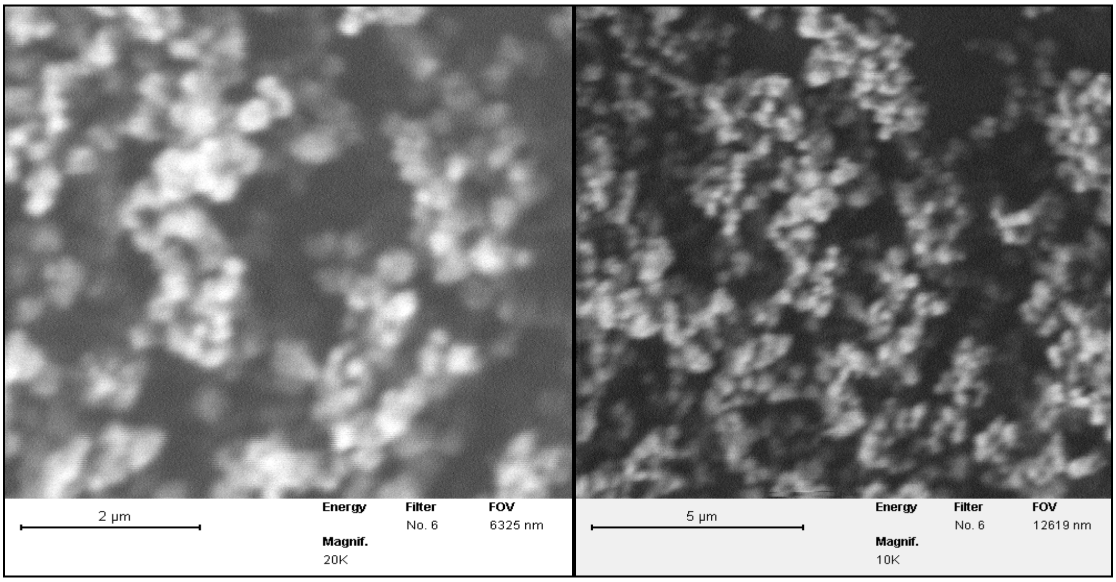


Figure 3.5 SEM images of HY-9(200) after 3 day aging, particles of 200 nm are produced

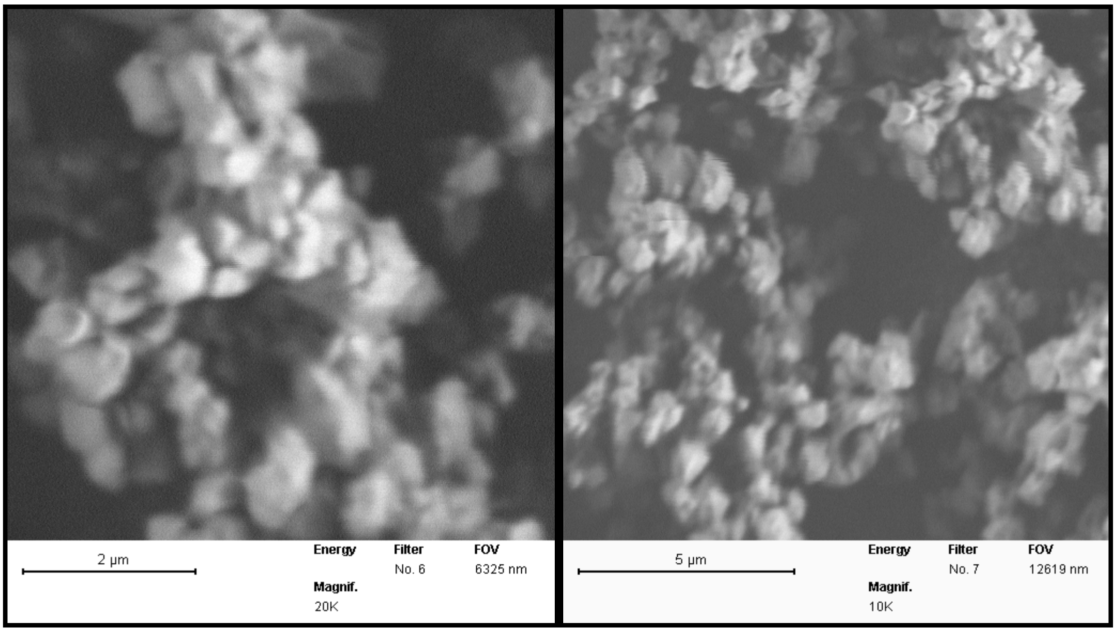


Figure 3.6 SEM images of HY-9(170) after 3 day aging in presence of surfactant, where particles of ~ 170 nm are produced

4. Results and Discussion

This chapter covers the results of two important aspects of our study. The first part discusses the results of model reactions over different zeolites catalyst tested in the lab scale reactor system starting from zeolites having different pore sizes, morphology, and SAR ratio. The effect of various reaction parameters on olefin conversion, and selectivity over highly active catalyst was also discussed. The second part includes the analysis, results and interpretation of experimental studies carried out on pilot plant reactor system.

4.1 Effect of Various Zeolites on the Alkylation of Benzene with 1-Decene

Table 4.1: Effects of various zeolites on alkylation of benzene with 1-decene

Catalysts	**1-Decene Conversion (%)**	**Product Distribution**		
		Monoalkylated[a]	**Heavy Products**[b]	**2-Phenyl Decane**
MORDENITE	40	99	8	55.4
MCM-22	53.68	99.66	3	66.87
H-β	51.57	99.74	2.8	58.86
HY-12	78.47	99.38	24.15	26.81
HY-30	83.57	99.03	7.78	29.63
HY-60	92.19	99.06	15.38	27.57
HY-9 (200)*	37.89	99.38	1.5	43.19
HY-9 (170)*	24.56	99.57	5.43	51.76

Reaction temperature; 100°C, amount catalyst; 5 gm, benzene to olefin molar ratio; 10:1, WHSA=1.5 gh-1, time on stream; 7 h, constant flow of nitrogen; 55 mL/min.

There will be small amounts of non-volatile products, which could not be detected by GC .

a Include 3, 4, 5, and 6 phenylalkane isomers (however, for 1-decene up to five isomers).

b Include decene dimers, dialkylbenzenes, alkyltetralenes and some other polymeric.

Table 4.1 summarizes the experimental results of alkylation of benzene with detergent range olefins; 1-decene over various zeolites (HY-12, HY-30, HY-60, and Mordenite-20, MCM-22(30), H-β (25) and in house prepared catalysts HY-9(200nm) and HY-9(170nm). Among the various zeolites screened, H-Y showed remarkable conversion compared to all other zeolites, due to presence of super cage which help the diffusion of reactant and product molecules easily on the active centres. However, this is at the expense of corresponding increase in the selectivity of the 2-phenyl isomer formation. Even H-β showed moderate activity although it is considered to be a stronger acid catalyst than H-Y [66]. This might be due to difficult diffusion of the reagents and products in to the active centre. Similarly the other large pore one-dimensional zeolite system also showed relatively lower conversion due to diffusion problem. The medium pore MCM-22 also showed comparable conversion and this can be attributed to the available 12-member-ring pockets (0.71 x 0.71 x 1.82 nm) on the external surface

Different zeolite catalysts show different selectivity towards 2-phenyl isomers, Mordenite, MCM-22 and BETA give higher selectivity compared to HY. Mordenite with unidirectional pore system leads to a larger selectivity to 2-phenyl isomer with increasing duration of time. The selectivity to the most desired 2-phenyl decane was found to increase with increased pore constraints.

The alkylation of benzene with olefins goes through a carbonium ion mechanism which involves two steps. Firstly, alkene interacts with the acid catalyst to form an alkylcarbenium ion. This carbocation undergoes rapid isomerization in varying degrees and finally attacks benzene in what is considered to be the rate determining step to form the product. The intermediate carbocation undergoing a series of fast hydride shifts produces isomeric ions. The hydride transfers, though very rapid, are not instantaneous [67], and therefore, some of the carbo-cation may react with aromatic ring before undergoing rearrangement [68]. In the case of 1-decene, five carbonium ions are possible. The relative stabilities of carbonium ions increase as the carbon number increases, for example, the least stable being the primary ion (1-position). In fact, due to its very low stability, the 1-phenyl isomer is not detected in the product.

In the present case this thermodynamic equilibrium is not probably reached. Greater 2-phenyl isomer content in the product mixture suggests a non-attainment of thermodynamic equilibrium. Under the present reaction conditions the intermediate carbocations from 1-

decene do not seem to attain equilibrium before they attack the aromatic ring or the rate of alkylation step is relatively faster than the rate of isomerisation of the intermediate to proceed to the most stable distribution. The stability of the carbocations increase in the following order: Primary (C_1) > Secondary (C_2) > Tertiary (C_3). The relative stabilities of the carbocations increase towards the center of the carbon chain, the least stable being the primary ion (C1-position). In fact due to its very low stability, the 1-phenylalkane is not at all detected. On the basis of this, one would expect the isomer content to increase with the carbon number (towards the center of the olefin chain). This is possible only if the thermodynamic equilibrium is reached before the carbonium ion attacks benzene. This is found to be so in the case of HF acid in which thermodynamic equilibrium is probably reached [68]. In all the cases there was formation of small amounts of tertiary alkylbenzene indicating the probabilities of skeletal isomerization of the intermediate ions. However, the rate of skeletal isomerization is low compared to the rate of alkylation or hydride shifts due to the mild reaction conditions. Actually, skeletal isomerization of 1-decene in presence of acid catalyst has been reported even at 100 ^{o}C and observation of small amounts of such reaction products in the mixture is not surprising.

4.2 Effect on Isomer Distributions

When the alkylation is carried out with 1-decene, the 2-phenyl, 3-, 4- and 5-phenyl isomer were found to be produced. The 1-phenyl isomer (where the phenyl group is attached to the terminal carbon of decene) was not detected due to the lower stability of the primary carbenium ion compared to the secondary carbenium ion. The 3-phenyl (3-ϕ) isomer is produced by the isomerisation of the C_2-carbenium ion to the C_3-carbenium ion which occur rapidly and same for C_4 and C_5 even at low temperature.

As the stability of $(C_2)^+$, $(C_3)^+$ and $(C_4)^+$ ions are nearly same, one should obtain all this ions in near equal amounts. i.e., the ratio of the 2-phenyl to 3-phenyl, (2-ϕ) /(3-ϕ) and 4-phenyl to 5-phenyl ((4-ϕ) /(5-ϕ)) should be less then and or equal to 1. However, results show that the 2-phenyl/3-phenyl ratio is always greater then 1. The reason for this is the competitive nature of the alkylation and olefin-isomerization reaction and the lack of any skeletal isomerisation at the conditions of the reaction. Even before the equilibration of the decene isomers (or carbenium ions) is achieved, alkylation of the reactant 1-decene to form the 2-phenyl isomer takes place [64].

Table 4.2: Isomer distribution over various zeolites

Catalyst	**C_{10} – Alkylbenzene distribution, (wt%)**			
	2-phenyl	**3-phenyl**	**4- phenyl**	**5- phenyl**
MCM-22	66.86	29.25	2.38	1.47
HY-12	26.81	27.21	23.10	22.86
HY-30	29.63	27.53	21.84	20.97
HY-60	27.57	27.44	22.29	22.68
HY-9 (200)*	43.19	24.41	16.57	15.80
HY-9 (170)*	51.76	24.36	13.28	10.53
Mordenite	55.4	20.2	14.54	9.9
BETA	58.86	25.79	9.09	6.24

Reaction Conditions: Temp. (°C) = 100; Press (kg/cm^2) = 10; WSHV (gh^{-1}) = 1.5; Benzene olefin (molar) ratio = 10; Data obtained at 7 hr on stream

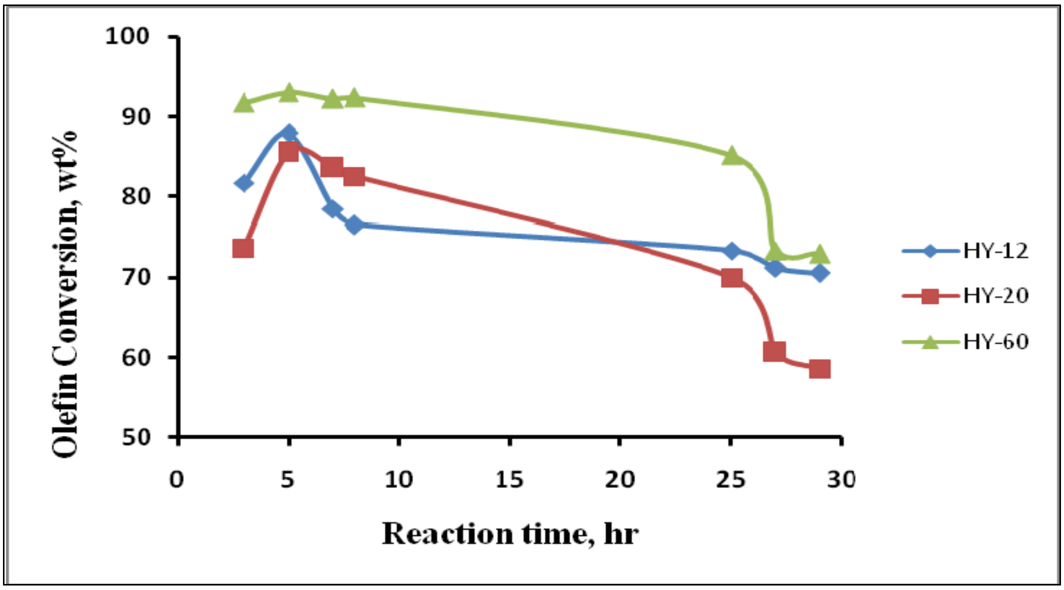


Figure 4.1. Effect of reaction time on olefin conversion over various HY zeolites

4.3 Effect of SiO_2/Al_2O_3 Ratios

It is well known that amount of acid sites will increase with decrease of SiO_2/Al_2O_3 ratios. Thus acidic sites of HY are expected to be in the following order HY-60 < HY-30 < HY-12 < HY-9. Ammonia TPD analysis also confirmed that HY-9 has huge amount of acid sites compared to HY-12, which is due to more aluminium in the frame work of zeolites. It is clear from Table 4.1 and Figure 4.1 that the olefin conversion follows in the reverse order, i.e. HY-60 showed better conversion at initial hour. There fore the acid sites must not be the only parameter that governs the overall activity. The acid site strength increases as the SiO_2/Al_2O_3 ratio increases, high acid strength HY-60 showed better conversion than other catalysts. However, the HY-9 showed relatively very lower conversion and higher 2-phenyl content than other samples, which might be due to presence of large excess of acid sites (from ammonia TPD). Under such situation the olefin undergoes polymerization / oligomerisation and as a result the active surface might get blocked which leads to less conversion [66].

Among all the H-Y zeolites, HY-12 was found to be better since its deactivation rate was minimal compared to other zeolites. Thus in order to find out the effect of various parameters like effect of time, temperature, various feed ratios on olefin conversion and 2-phenyl content selectivity we have chosen HY-12 for further studies.

Our aim was to arrive at a stable catalyst for alkylation of benzene with long chain olefin, which can yield complete olefin conversion with 2-phenyl isomer in the range of 25 to 30%. The product having 2-phenyl isomer content in the above range gives better emulsibility and solubility characteristics for detergent.

4.4 Alkylation of Benzene with 1-Decene over H-Y-12 Catalysts at Different Reaction Conditions

Liquid-phase reactions were performed under constant flow of nitrogen. The effect of reaction temperature, catalyst loading, and benzene to olefin molar ratio were examined in order to optimize the conversion of olefin and selectivity to the monoalkylated product or more precisely the 2-phenyl isomer formation by using HY-12 catalysts.

4.4.1 Effect of Olefin to Benzene Molar Ratio

Table 4.3 Effect of BOR Molar ratio on Olefin Conversion

Time on stream	Olefin Conversion			
	BOR 5:1	**BOR 10:1**	**BOR 15:1**	**BOR 20:1**
3	56.95	81.68	69.33	71.20
5	49.65	87.89	70.83	70.41
7	34.95	78.47	84.5	76.22
8	34.26	76.52	85.5	80.60
18	31.47	73.36	86.73	88.31
20	25.21	71.15	77.83	85.38
22	24.86	-	81.5	81.67

Reaction Conditions: Temp. (^oC) = 100; Press (kg/cm^2) = 10; WSHV (gh^{-1}) = 1.5; Data obtained at 7 hr on stream

Table 4.3 and Figure 4.2 present the effect of molar ratio of feed Benzene to olefin ratio on the olefin conversion. As the benzene to olefin ratio (BOR) increased from 5 to 10, the conversion of olefins increased almost twofold. The presence of excess benzene leads to solvation effect and dilute the olefin concentration, which help to efficient interaction of olefin with active catalytic surface. Further, increase of benzene to olefin ratios (15 & 20), the conversion of olefin reaches maximum and there is no major change observed with reaction time.

At lower benzene to olefin molar ratio 5 the improvement in the 2-phenyldecene with time is clearly seen from Table 4.4 and Figure 4.2. The presence of more olefin in the feed and its strong interaction with active catalyst surface leads to coke formation. The deposited coke covers the catalyst surface. It practically prevents the diffusion of relatively bulk isomerised products viz., 3, 4, 5 or 6-phenyldecane. This could also be due to transalkylation reaction between benzene and didecylbenzene and tridecylbenzene in the zeolite pore mouth [69]. The increase in the 2-phenyl isomer production is strongly supported by a corresponding decrease in the dialkylate formation with time.

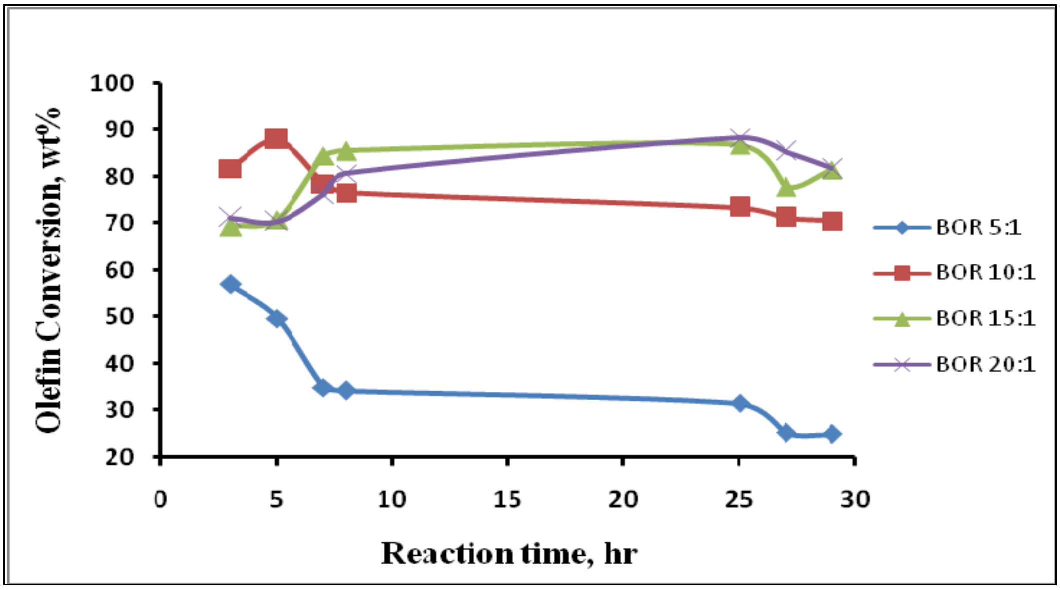


Figure 4.2. Effect of BOR Molar ratio on Olefin Conversion over zeolite-Y HY-12

Table 4.4 Effect of Benzene:1-Decene Molar ratio on 2-Phenyl isomer

Time on stream	2-Phenyl Isomer			
	BOR 5:1	**BOR 10:1**	**BOR 15:1**	**BOR 20:1**
3	30.96	28.56	30.72	30.39
5	30.15	27.35	30.82	30.25
7	30.26	26.81	29.31	30.12
8	30.50	27.54	28.29	33.32
18	37.53	28.41	28.33	27.41
20	39.59	27.52	28.81	30.00
22	40.16	27.99	30.82	30.19

Reaction Conditions: Temp. (°C) = 100; Press (kg/cm^2) = 10; WSHV (gh^{-1}) = 1.5; Data obtained at 7 hr on stream

Fig. 4.3 and Table 4.5 show influence of molar ratio of the reactants on the conversion and selectivity of the alkylation reaction. Initially conversion increases with increase of BOR 5 to 15, after that it decreases with increase in benzene to olefin molar ratio from 15 to 20. However, selectivity for the 2-phenyl isomer increases from 27.5% to 33.3% on increasing the molar ratio from 1:10 to 1:20, and the formation of heavy isomers decreases from 21% to 4.9%. Increase in the 2-phenylalkane selectivity could be explained in terms of solvation effect of benzene in higher molar ratios. The presence of excess benzene, the intermediate carbonium ion can easily react with benzene rather than undergoing isomerization, which ultimately results in greater formation of 2-phenyldecane.

Table 4.5. Effect of BOR Molar ratio on product distribution over zeolite-Y HY-12

Molar Feed ratio	**Conversion, %**	**2-phenyl isomer, wt %**	**HA/LAB, wt/wt %**	**Linearity, wt%**
5	34.27	30.50	14.98	99.22
10	76.57	27.54	21	9938
15	85.5	28.29	12.58	98.89
20	80.6	33.32	4.96	98.94

Reaction Conditions: Temp. (^oC) = 100; Press (kg/cm^2) = 10; WSHV (gh^{-1}) = 1.5; Data obtained at 7 hr on stream

The initial activity and deactivation rate (decrease in conversion with time) of the different molar ratio is found to be different. For lower molar feed ratio catalyst deactivates very fast but for relatively high molar feed ratios the catalyst has high initial activity and low deactivation. In other words, increase in BOR 5 to 20, the rate of deactivation decreases and it shows that the activity of catalyst remains stable for long time.

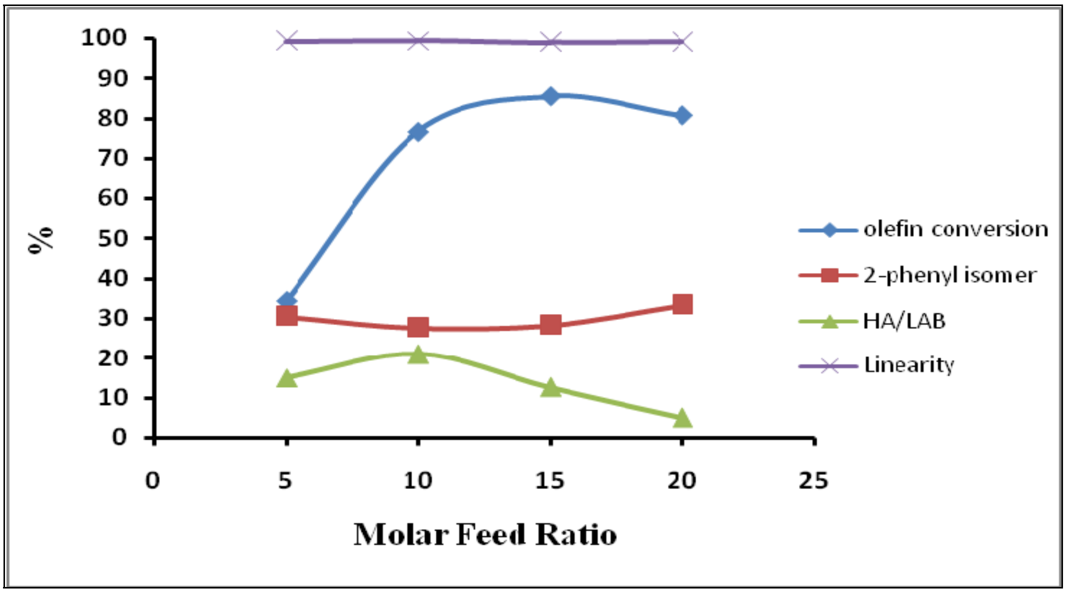


Figure 4.3 Effect of BOR molar ratio on product distribution over zeolite-Y HY-12

The interaction of the olefin with the acid catalyst leads to formation of an alkylcarbenium ion which undergoes rapid isomerisation to varying degree.The isomeric alkyl carbenium ions and then attack benzene, forming mono alkylbenzene. At higher BOR like 20 due to availability of excess benzene which restricts the probability of competitive reaction of carbenium ion like olegomerization and polymerization etc. This results in formation of lower HAB products.

4.4.2 Effect of WHSV

Alkylation of benzene with 1-decene was also performed at different space velocity ranging form 1.0-2.0 using BOR ratio of 10, at the temperature of 100 °C. The results are summarized in Table 4.6. At lower WHSV (1 and 1.5) the olefin conversion and 2-phenyl content selectivity does not vary much. Further the catalytic activity was found to be steady, since olefins have enough residential time to interact with active catalytic surface. However, when the WHSV increases to 2.0 the conversion decreases considerably over the reaction period, due relatively less contact time of olefin with active surfaces. Therefore WHSV about 1.5 gh^{-1} is found to be ideal to have better olefin conversion with appropriate 2-phenyl content.

Table 4.6 Effect of WHSV for alkylation of benzene with 1-decene over HY-12

WHSV	Flow Rate, ml/min	Conversion, %	2-phenyl isomer, wt %	HA/LAB, wt/wt %	Linearity, wt%
1	0.11	82.10	26.64	99.61	6.76
1.5	0.16	87.68	26.81	99.38	24.14
2	0.21	85.78	29.24	99.06	8.61

Reaction Conditions: Temp. (^{o}C) = 100; Press (kg/cm^2) = 10; Benzene olefin (molar) ratio = 10; Data obtained at 7 hr on stream

4.4.3 Effect of Reaction Temperature

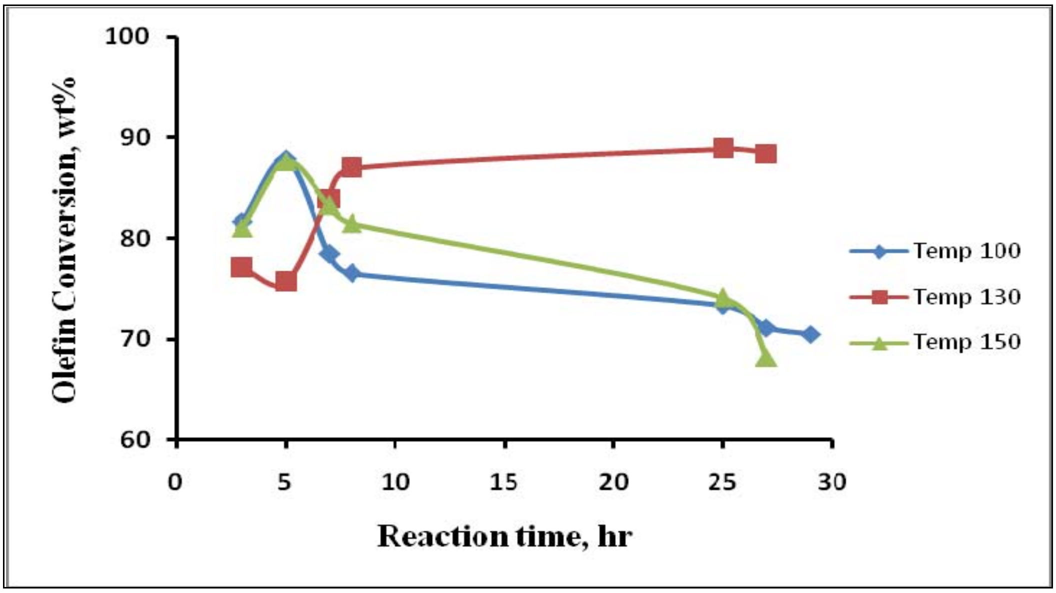


Figure 4.4 Effects of temperature over zeolite HY-12

The HY-12 catalyst was further studied at different reaction temperature on model reaction keeping WHSV (1gh^{-1}) and BOR (10:1) constant and the results are depicted in Figure 4.4. It can be seen from Figure 4.4 that the olefin conversion increases with increase of reaction temperature from 100 to 130 ^{o}C and reaches a maximum and the conversion remains steady over the period of time. However, further increase of reaction temperature from 130 to 150 oC results lower conversion and continuos decrease of conversion with time, indicating fast deactivation of catalysts due to side reactions viz., polymerizaiton & oligomerization of olefin [70].

After systematic evaluation of HY-12 samples at lab scale for the model reaction (benzene alkylation with 1-decene), it was identified that BOR of 15, temperature of around 130 ^{o}C, with WHSV 1.5 g.h^{-1} was found to be best suitable condition to obtain maximum olefin conversion, desired 2-phenyl content with less heavy aromatic content. It is clearly seen from lab scale studies that zeolite HY-12 catalyst is found to be promising candidate for LAB process, necessitating further studies on HY-12 catalysts in pilot plant, with special emphasis on the acidity and structural modification of the zeolites HY-12.

4.5 Pilot Plant study

To get better information and more reliability in the area of catalytic stability and activity in a commercial operation conditions, we have taken special interest and continue the study on catalytic activity of HY-12 in pilot plant, using paraffin contains about 12 wt. % of mixed long chain olefins (C_{10}-C_{14}). The relationship between activity and selectivity of catalyst and its porous nature will have considerable attention from investigators of both industrial and academic background. To meet the commercial interest and industrial requirement, we have planed to do some more study with pilot plant reactor set up in large scale. We have chosen three catalysts viz., HY-12, divalent metal exchanged (Zn^{2+} and Mg^{2+}) HY-12. In order to reduce the heavy aromatic formation, we have modified the acidity by ion exchange process using Zn and Mg salts. Initially HY-12 catalyst was tested under different reaction conditions like temperature, WHSV and different mole ratio again in pilot plant conditions using mixed long chain olefins (C_{10}-C_{14}) to evaluate the stability, selectivity and life of the catalyst.

4.5.1 Effect of Temperature

Table 4.7 and Fig. 4.5 show the effect of reaction temperature in the liquid-phase alkylation of benzene with 1-decene. Reaction temperature was varied between 120 ^{o}C and 150 ^{o}C over HY-12 zeolite. The conversion of olefins increases slightly with increase in the reaction temperature (98.1% at 120 ^{o}C increased to 99.6% at 130 ^{o}C) and reaches maximum and remain the same over further increase of temperature up to 130 ^{o}C.

Table 4.7 Effect of reaction temperature on productt distribution over HY-12 at pilot plant

Temperature, °C	**Conversion,%**	**2-Phenyl Isomer, wt%**	**HA/LAB, wt/wt %**	**Linearity, wt%**
120	98.1	21.70	10.77	92.55
130	99.5	21.05	15.27	94.20
140	99.44	21.05	17.34	90.30
150	99.03	20.96	23.71	91.62

Conditions; Press (kg/cm^2) = 10; WSHV (gh^{-1}) = 1.5; Benzene olefin (molar) ratio = 15

However, at higher temperature the heavier aromatic formation increases linearly, thus HA/LAB ratio also remains high. At higher temperature, due to high activity of carboneium ion formed during the reaction leads to formation of dialkyl, trialkyl benzene. Further, there is increased probability of catalytic cracking, rapid equilibration of the olefin isomer and easy diffusion of the bulkiest LAB isomers which leads to higher heavy aromatic content. Although the olefin conversion was not varying much with increase in reaction temperature for optimum selectivity, it is found that about 130 °C is the suitable reaction temperature.

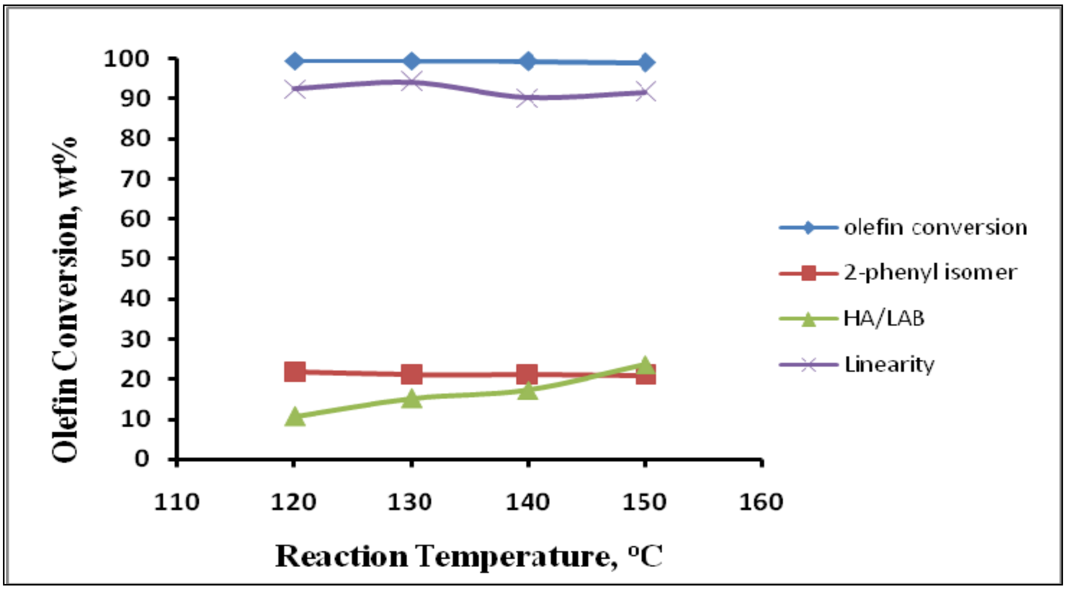


Figure 4.5 Influence of reaction temperature during the alkylation of benzene with long chain olefin mixture over HY-12 zeolite

4.5.2 Effect of Feed Flow Rate or WHSV

The influence of reactant feed flow rate (WSHV) on the conversion in the alkylation with mixed olefin is present in figure 4.6. The increase in WHSV from 1.0 to 1.5 the olefin conversion and also improved the linearity. Further, 2-phenyl content and HA/LAB also remain same. Further, increase of WSHV the olefin conversion decrease considerable due to fast diffusion of intermediate carbonium ion formed from olefin mixture on the active surface of zeolite-Y. And also considerable increase in HA/LAB ratio, the reason is not very clear may be the carbonium ion formed may go for secondary reaction in the liquid phase thus HA/LAB content increases [71].

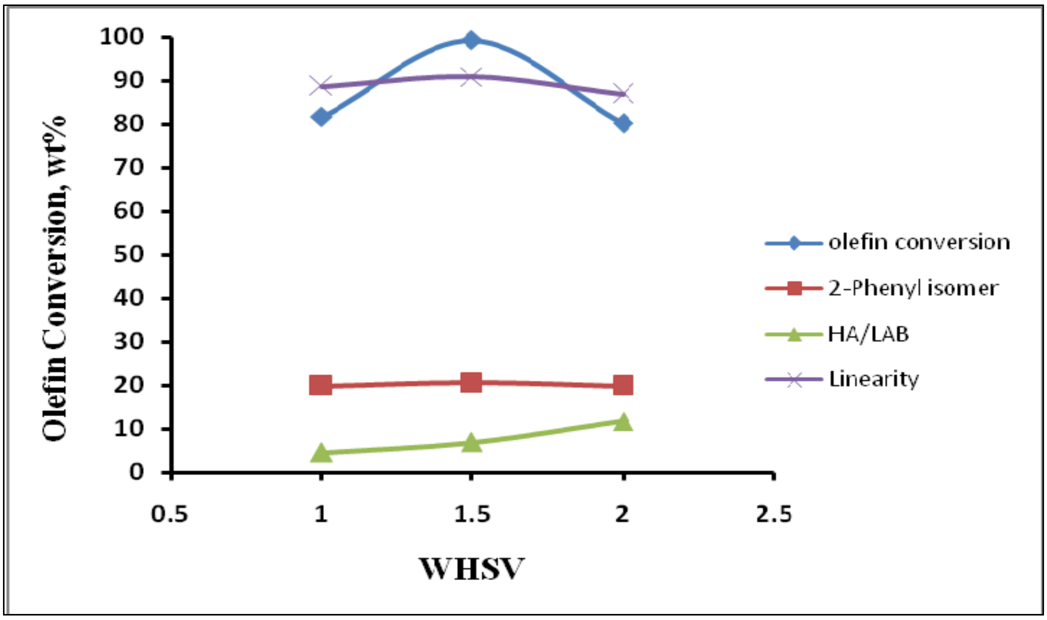


Figure 4.6 Effect of WHSV on product distribution over zeolite-Y (HY-12).

4.5.3 Catalytic Activity of Mg Ion Exchanged HY-12 (MgHY-12) at Different Temperature

Table 4.8 shows the effect of various reaction temperatures over MgHY. Olefin conversion and 2-phenyl isomer remain same irrespective of the reaction temperature. However, the linearity of the product decreases with increase of temperature, which is similar to the case of pure HY-12 sample. Importantly, unlike HY-12 the formation of heavy alkyklates is drastically controlled over MgHY-12 (Figure 4.7). This might be due to occupation of Mg on the strong acidic sites, which normally favour secondary reactions. The blocking of strong acidic sites by Mg is highly helpful for the reduction in heavy alkylate formation.

Table 4.8 Effect of Temperature on product distribution over MgHY-12

Temperature, °C	**Conversion,%**	**2-Phenyl Isomer, wt%**	**HA/LAB, wt/wt %**	**Linearity, wt%**
120	99.33	21.09	5.36	90.82
130	99.27	20.477	4.68	89.63
140	99.02	20.44	5.42	86.85
150	98.28	20.27	6.14	85.79

Reaction Conditions; Press (kg/cm^2) = 10; WSHV (gh^{-1}) = 1.5; BOR (molar) ratio = 15

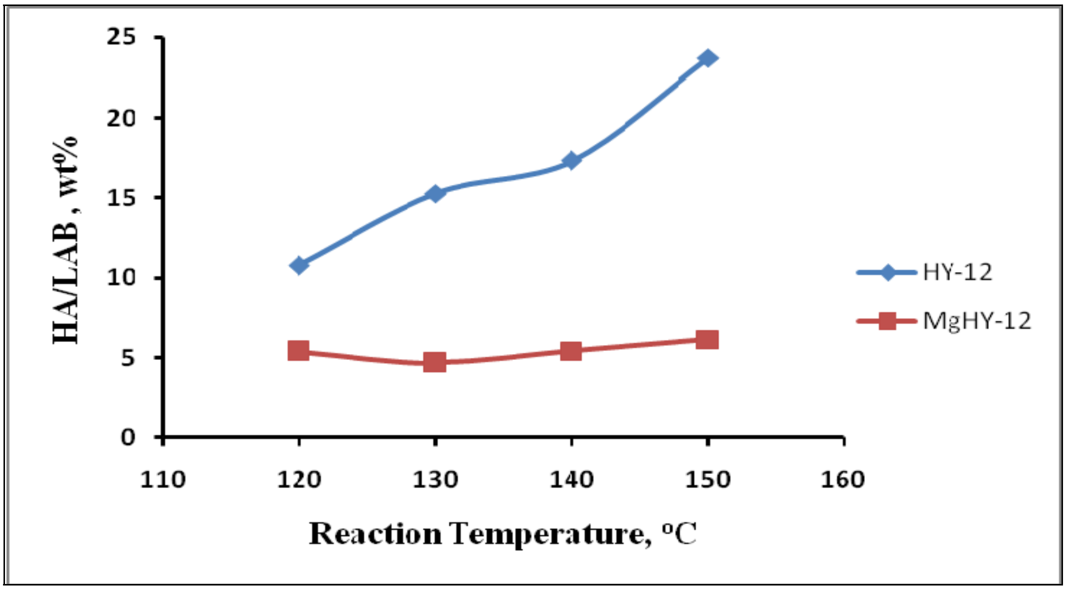


Figure 4.7 HA/LAB content over HY-12 and MgHY-12 samples at different temperatures

Table 4.9 summarizes the conversion and product distribution of LAB alkylation reaction over HY-12, Mg and Zn exchanged HY-12 samples. The 2-phenyl content is not much affected with different ion-exchange cations. However, the catalytic conversion of olefin reduces considerably in Zn exchanged HY-12 samples, which might be due to considerable formation of Lewis acid sites, which might favour secondary reaction thus reducing the olefin conversion. However, the heavy aromatics formation reduces drastically in both Mg and Zn exchanged zeolite-Y catalysts.

Table 4.9 Effect of Temperature on product distribution over acidity modified zeolite-Y

Catalysts	**Conversion, %**	**HA/LAB, wt/wt %**	**Linearity, wt%**	**2-Phenyl Isomer, wt%**
HY-12	99.5	1.91	21.05	99
MgHY-12	99.4	0.566	22.1	99.2
ZnHY-12	80	0.543	19.48	98

Reaction Conditions; Temperature (^oC) = 130; Press (kg/cm^2) = 10; WSHV (h^{-1}) = 1.5; Benzene olefin (molar) ratio = 15

4.5.4 Effect of Dienes Content in the Feed Mixture

Figure 4.8 illustrates the alkylation of benzene with paraffin mixture contain with less diolefin contain feed as well as diolefin rich reactant feed over HY-12 keeping other parameters constant such as temperature 130 ^oC, BOR of 15, and WHSV of 1.5 gh^{-1}. As the concentration of diolefin in the paraffin mixture (olefin feed) increases from 0.1 to 0.7 wt %, the conversion of olefins decreases to almost half. Further with extended time on stream the catalytic activity decreases rapidly and reaches to minimum level (about 25 %), implying substantial effect on the yield of linear alkylbenzenes and also the relative stability of the sample of catalyst HY-12. The observed fast deactivation of HY-12 over diolefin rich reactant feeds is mainly due to higher level of coke formation, which is clearly seen in Figure 4.9. The TGA of HY-12 catalysts after carrying out the reaction using normal olefin feed and diolefin rich olefin feed is shown in Figure 4.9. The catalyst used in presence of di-olefin rich reactant feed shows about 24 wt.% weight loss compared to catalyst used in presence of normal olefin feed (17 wt.%). Thus the presence of diolefin rich reactant feed favour secondary reaction (polymerization/oligomerization and secondary alkylation reaction) and gives more diphenylalkanes, alkyltetralins, and alkylindans [72] than alkylation of benzene and hence reduces the olefin conversion, LAB yield.

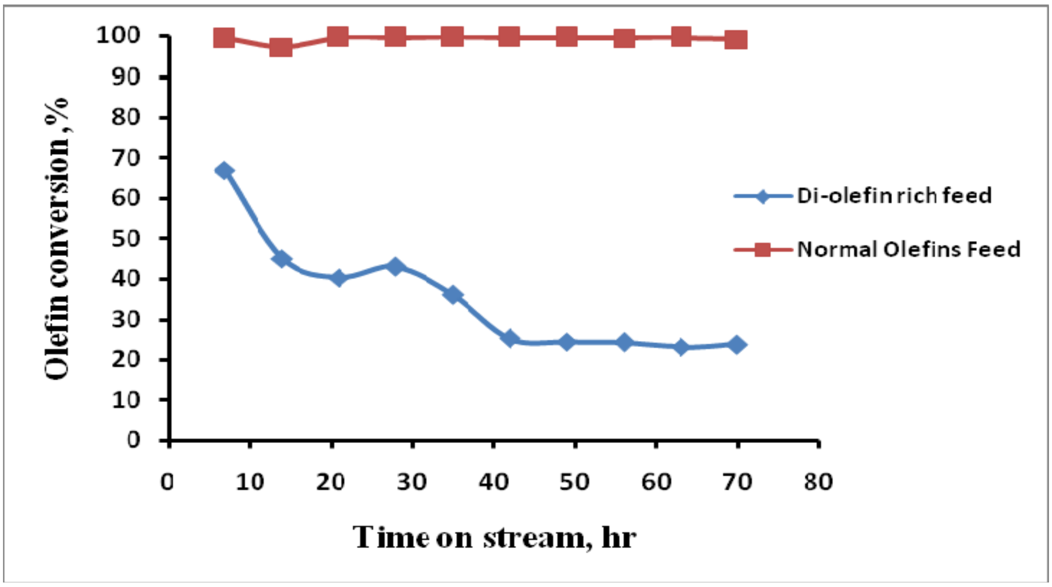


Figure 4.8. Effect of normal olefin (0.1 wt.% of di-olefin) and di-olefin rich olefin feed (0.7 wt.% di-olefin) on catalytic conversion of olefin over HY-12 zeolites.

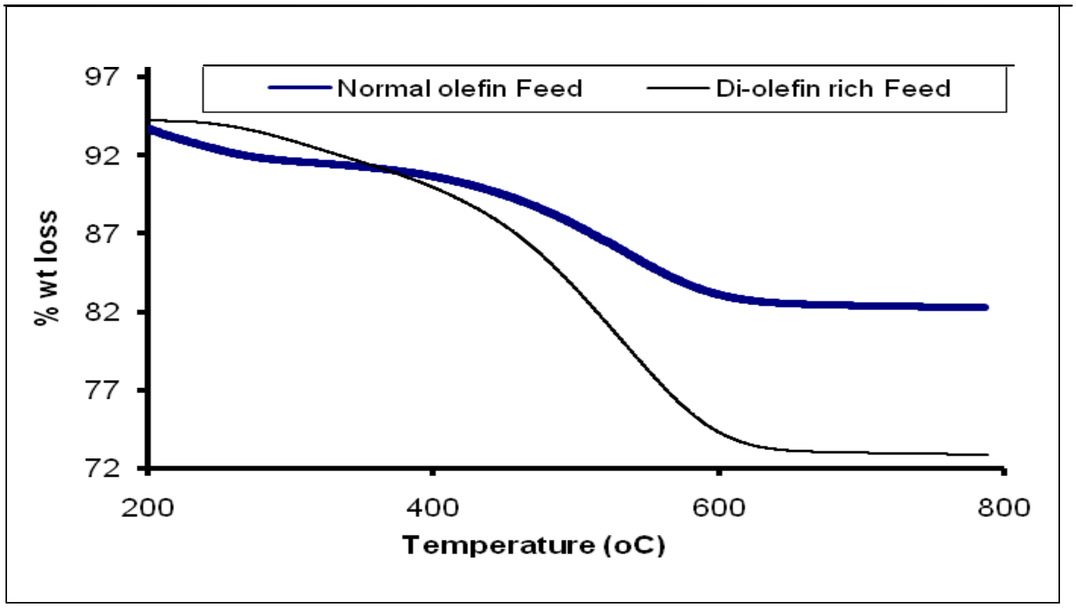


Figure 4.9 TGA analysis of catalysts (HY-12) used in presence of Normal Olefins Feed and Di-olefins rich Feed.

4.5.5 Life of Various Zeolite-Y Catalysts for the LAB Processes

The influence of process parameter on the life of HY-12 based catalyst in the alkylation with mixed olefin is studied. From this study we can say that increasing the temperature beyond 130 ^{o}C does impact the life of the catalyst. Similarly, operating at low benzene to olefin ratio lowers the life of the catalyst.

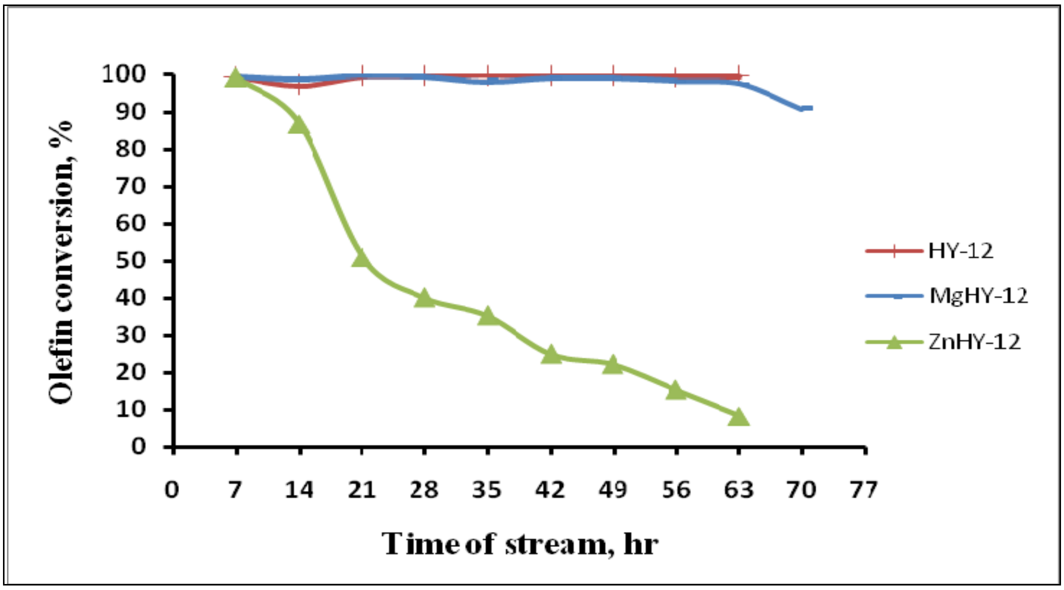


Figure 4.10 Life of various Zeolite Y catalysts for LAB processes

In order to see the life of various catalysts used for the LAB processes, we have studied the series of catalysts (HY-12, MgHY-12 and ZnHY-12) over the period of 72 h continuously under the optimum reaction conditions (T= 130 °C, WHSV = 1.5 $g.h^{-1}$, BOR = 15) and the results are presented in Figure 4.10. It is clear from the figure that both HY-12 and MgHY-12 showed steady activity throughout the reaction periods. However, Zn-HY-12 showed continuous decrease of olefin conversion and it reaches almost to zero by 64 h. Thermal analysis of the used catalysts showed two major significant weight loss at ca. 200 & 500 °C. The lower temperature weight loss can be attributed to the adsorbed products and the higher temperature weight loss is possibly due to alkenes oligomers which might block the channel of zeolite pores. Although HY-12, and MgHY-12 showed no loss of catalytic activity over the period of 72 h, but the thermal analysis showed considerable weight loss from coke formation. The coke can be regenerated by burning in air around 550 °C and then the catalytic activity may be regained. However, in the case of ZnHY-12 the thermal analysis showed large excess of coke content. This coupled with possible blockage of pore by bigger Zn^{2+} cation can further reduce the catalytic activity significantly thus explaining the performance over extended time on stream.

5. Conclusions and Future Path

Various zeolites were screened for the alkylation of benzene with 1-decene as a model reaction for LAB processes. The following inferences could be drawn from our lab scale and pilot-plant studies.

Among the various zeolites scanned for the model reaction, the large pore zeolite-Y showed superior conversion with desired 2-phenyl isomer selectivity. The other large pore zeolites such as Mordenite, Hβ and medium pore MCM-22 showed comparable conversion with high selectivity towards 2-phenyl isomer compared to zeolite-Y and commercially used HF catalyst. The higher selectivity of 2-phenyl isomer over Mordenite, Hβ and medium pore MCM-22 was mainly due to increased pore constraints.

The optimum condition for LAB process using model reaction to get maximum olefin conversion with desired 2-phenyl isomer content having minimum heavy aromatics formation is at the temperature of 130 ^{o}C, WHSV = 1.5 g.h^{-1}, BOR = 15. Linearity of mono alkyl benzene is also in the range of 97-99% with desired 2-phenyl isomer content. This shows the better product quality and superior catalytic activity of HY as compared to HF catalyst.

Further, studies on pilot plant using commercial olefin feeds containing mixed long chain olefin (C_{10}-C_{14}), confirm the potential of zeolite-Y for the LAB processes. The modification of HY by Magnesium and Zinc reduces the acidic sites, which helps to reduce the heavy alkylate formations. The MgHY-12 catalyst for LAB synthesis shows good performance in terms of olefin conversion and stability in the operation. The coke formation also found to be less throughout the reaction periods.

However, the modification with Zinc doesn’t help much on improvement in the selectivity and activity of catalyst. The zinc modified HY showed fast decrease in olefin conversion indicating that the introduction of zinc created the Lewis acid sites which reduced the total conversion and also triggered secondary side reaction.

Further, it was found that the diolefin content in the feed play a significant role on the catalysts deactivation. So, the diolefin content in the olefin feed mixture should be in the range of 0.1 wt%, for the better catalytic life.

In summary Zeolite-Y and magnesium exchanged Zeolite-Y found to be ideal candidate for the LAB production in environment friendly manner.

Future Path

1. Since Mg^{2+} exchanged Zeolite Y showed improved performance with respect to heavy alkylate formation, it is proposed that other elements of Group II such as Calcium, Strontium & Barium can also be ion exchanged on HY and their performance can be studied.

2. Studies on different modes of regeneration of the catalyst such as hot hydrogen stripping, benzene wash and controlled coke burning can be attempted to establish efficiency of regeneration and ascertain reuse of the catalyst.

References

1. J. March, *Advanced Organic Chemistry reactions, mechanisms and structure* (3rd ed.). New York: John Wiley & Sons, inc., (1885).

2. H.G. Franck, J.W. Stadelhofer, *Industrial Aromatic Chemistry*, Springer, Berlin, (1988).

3. Chem. System, *Process Evaluation Research Planning* (93S10), Tarrytown, New York, 1995.

4. J.L.G. de Almeida, M. Dufaux, Y. Ben Taarit, C. Naccache, *J, Amer. Oil Chem. Soc*. 71 (7) (1994) 675.

5. P. N. Borutski, E. G. Kozlova, N. M. Podkletnova, N. D. Gil'chenok, B. C. Sokolov, V. A. Zuev, A. A. Shatovkin,*Petroleum Chemistry*, 47(4), (2007) 250-261.

6. Report Abstract ,lab,PERP 07/08 S7,February 2009 by chemsystem.com

7. Joseph A. Kocal, Bipin V. Vora, Tamotsu Imai, *Production of Linear Alkylbenzenes*, Applied Catalysis A: General 221 (2001) 295–301

8. T. Fritsch, S. Ozemen, S. Raghuram, et al. *New Tchnologies for Production of Detergent Intermediates*,third CESIO International Surfactant Congress, London, 1992.

9. J. Berna, A Moreno, A. Banerji, et al., *Growth and Developments in LAB Technologies: 30 Years of Innovation and More to Come,* World Surfactant Conference, Switzerland, 1993.

10. P.G. Bannov, Oil Refining Processess, volume II, Moscow, 1998.

11. Proceedings of UOP conference on Synthetic Detergents, Russia, 1998.

12. ARCO Technology Inc., Hydrocarbon Processing 64 (11) (1985) 127.

13. P.R. Pujado, *Linear Alkylbenzene Manufacture: Handbook of Petroleum Refining Processes,* 1997, pp. 1.53–1.66.

14. R.E. Berg, B.V. Vora, *Encyclopedia of Chemical Processing and D*esign, Vol. 15, Marcel Dekker, New York, 1982, pp. 266–284.

15. Jacobs, P.A., and J.A.Martens, *Introdution to Zeolite Science and Practies,* edited by V. Vann Bekkum, E.M. Flanigen and J.C. Janesen, Elsevier, 1991.

16. Anon.,*Krik-Othmer, Encyclopedia of Chemical Technology,* 2nd edition, Volume 1, 1963.

17. Patikins, S.H., and B.S. Friedman, *Friedel-Crafts and Related Reactions,* Interscience Publishers, Volume 2, Chapter14.

18. Roberts, R.M., and A.A. Khalaf, *Friedel-Crafts Alkylation Chemistry,* Marcel Dekker, New York, 1984.

19. Davidsohn, A.S., and B. Milwidsky, *Synthetic Detergents*, Longman Scientific & Tachnical, Essex, 7th edition, 1987.

20. Holtzman, S., and B.M. Milwidsky, *Soap Chemistry Spec.:64., 1986*

21. A. Keshavaraja, K.R. Srinivasan, Chem. Ind. Dig. 8 (4) (1995) 127–129.

22. P.B. Venuto, A.L. Hamilton, P.S. Landis, J.J. Wise, J. Catal. 5 (1996) 272.

23. Ed. By van Beckum, H. et al. *Introduction to zeolite science and practice*.(1991). Amsterdam: Elsevier.(Studies in Surface Science and Catalysis, Vol 58,13).

24. Hagen, Jens. (1999). *Industrial Catalysis, A Practical Approach*,230. Weinheim: Wiley-VCH.

25. Hagen, Jens.(1999). *Industrial Catalysis, A Practical Approach*.Weinheim: Wiley-VCH.

26. www.wikipedia.org/wiki/Zeolites

27. S. M. Csicsery, Zeolites, 4, 202 (1984).

28. P. N. Borutskii, in *New Chemist and Engineer's Handbook: Raw Materials and Products of Organic and Inorganic Industrial Chemistry*, Ed. by Yu. V. Pokonova and V. I. Strakhov (NPO Professional, Mir i Sem'ya, St. Petersburg, 2002), part 1, p. 873 [in Russian].

29. J. Germain, *Catalytic Conversion of Hydrocarbons*, (Academic, London, 1969; Mir, Moscow, 1972).

30. C. Thomas, *Catalytic Processes and Proven Catalysts* (Academic, New York, 1970; Mir, Moscow, 1973).

31. M. A. Dalin and V. A. Sidorov, in *Petroleum Chemist's Handbook*, Ed. by S. K. Ogorodnikov (Khimiya, Leningrad, 1978) vol. 2 [in Russian].

32. S. V. Adel'son, T. P. Vishnyakova, and Ya. M. Paushkin, *Engineering of Petrochemical Synthesis* (Khimiya, Moscow, 1985) [in Russian]

33. A. Gaile, O. M. Varshavskii, and V. E. Somov, *A Handbook of Aromatic Hydrocarbons: Isolation, Application, and Market*, (Khimizdat, St. Petersburg, 2000) [in Russian].

34. *Handbook of Modern Petroleum Refining Processes* (2000); Neftegaz. Tekhnol., No. 3, 94 (2001).

35. N. N. Lebedev, *Chemistry and Technology of Basic Organic Synthesis* (Khimiya, Moscow, 1988) [in Russian].

36. B. R. Serebryakov, R. M. Masagutov, V. G. Pravdin, et al., *New Processes of Organic Synthesis*, Ed. by S. P. Chernykh (Khimiya, Moscow, 1989) [in Russian].

37. N. G. Grigor'eva, G. N. Kirichenko, M. F. Bondarenko, et al., in *Recent Advances in Petroleum Refining and Petroleum Chemistry*, Abstracts of Papers of

Republican Scientific and Technical Conference (Ufa, 1981), p. 120 [in Russian].

38. K. I. Patrilyak, Yu. N. Sidorenko, and V. A. Bartyshevskii, *Alkylation on Zeolites* (Naukova Dumka, Kiev,1991) [in Russian].

39. A. N. Sachanen and A. A. O’Kelly, Ind. Eng. Chem. **33**, 1540 (1941).

40. T. L. Natanson and M. Ya. Kogan, Zh. Fiz. Khim. **71** 381 (1943).

41. V. V. Sukhovertov and I. I. Martsin, *Proceeding of VII Petrochemical Symposium* (Kiev, 1990) [in Russian].

42. T. H. Johnson, US Patent No. 4, 524229 (1985).

43. T. H. Johnson, US Patent No. 4, 463207 (1984).

44. I. Y. Ryu, AU Patent No. 5, 10893 (1980).

45. S. M. Kowach, US Patent No. 4, 489213 (1984).

46. A. Gieysztor, A. Malinowski-Krzywski, and B. Zelinski, PL Patent no. 106550 (1980).

47. Ahmed K. Aboul-Cheit, Alfat F. Moustafa, and Pamri M. Habub, Erdol und Kohle-Erdgas Petrochem. **10**, 462 (1985).

48. B. Tejero, J. Luis, and M. Pat. Danvila, ES Patent No. 2007545 (1989).

49. T. J. L. Berna and D. A. Moreno, US. Patent No. 5146026 (1992).

50. T. J. L. Berna and D. A. Moreno, US Patent No. 5157158 (1992).

51. US Patent No. 5003121 (1991).

52. S. Leite, L.Dieguez, and R. A. S. San Gil de Menezes, Quim. Nova 23, 34 (2000).

53. E. D. Rostanina, L. D. Konoval’chikov, B. K. Nefedov, and N. N. Rostanin, *Proceedings of Fourth All-Union Conference on Application of Zeolites in*

Catalysis (Nauka, Moscow, 1989), p. 114 [in Russian].

54. B. Wang, C. W. Lee, T.-X. Cai, and S.-E. Park, Bull. Korean Chem. Soc. **22**, 1056 (2001).

55. J. F. Knifton, P. R. Anantaneni, and P. E. Dai, US Patent No. 5847254 (1998).

56. K. Arata, Adv. Catal **7**, 165 (1990).

57. M. T. Pope, in *Heteropoly and Isopoly Oxometalates* (Springer Verlag Berlin, 1983).

58. M. Misono and T. Okuhara, CHEMTECH, November, 23 (1993).

59. B. B. Bardin and R. J. Davis, Top. Catal. **6** 77 (1998).

60. Lee, W.Y.et. al. (1993). Alkylation of toluene over double structure ZSM-5 type catalyst covered with a silicate shell. *Applied Catalysis A: General (96), 151-161.*

61. R.T. Sebulsky, A.M. Henke, Ind. Eng. Chem. Process Des. Dev. 10 (1971) 272.

62. Q.N. Le, D.O. Marler, J.P. Mc Williams, M.K. Rubin, J. Schim, S.S. Wong, US Patent 4,962,256.

63. S. Sivasanker, A. Thangaraj, J. Catal. 138 (1992) 386.

64. S. Sivasanker, A. Thangaraj, R.A. Abulla, P. Ratnasamy, in: *Proceedings of the International Congress on Catalysis*, NewFrontiers in Catalysis, Vol. 75, Elsevier, Amsterdam, 1992, p. 397.

65. Bromine Number of Petroleum Distillates and Bromine Index of Industrial Aromatic Hydrocarbons-Potentiometric Method, UOP Method 304-59.

66. Y. Cao, R. Kessas, C. Naccache, Y. Ben Taarit, Appl. Catal. A: Gen. .

67. P.M. Price, J.H. Clark, K. Martin, D.J. Macquarrie, T.W. Bastock, Org. Process

Res. Dev. 2 (1998) 221–225.

68. M. Freemantle, Chemical and Engineering News, 30 March 1998, pp. 32–37.

69. Bejoy Thomas, Bibhuti B. Das, *Rare Earth Exchanged (Ce3+,La3+ and RE3+) HY Zeolite as sold acid catalysts for the synthesis of linear alkyl benzene*, MIcroporous and Misoporous Materials 95 (2006) 329 338.

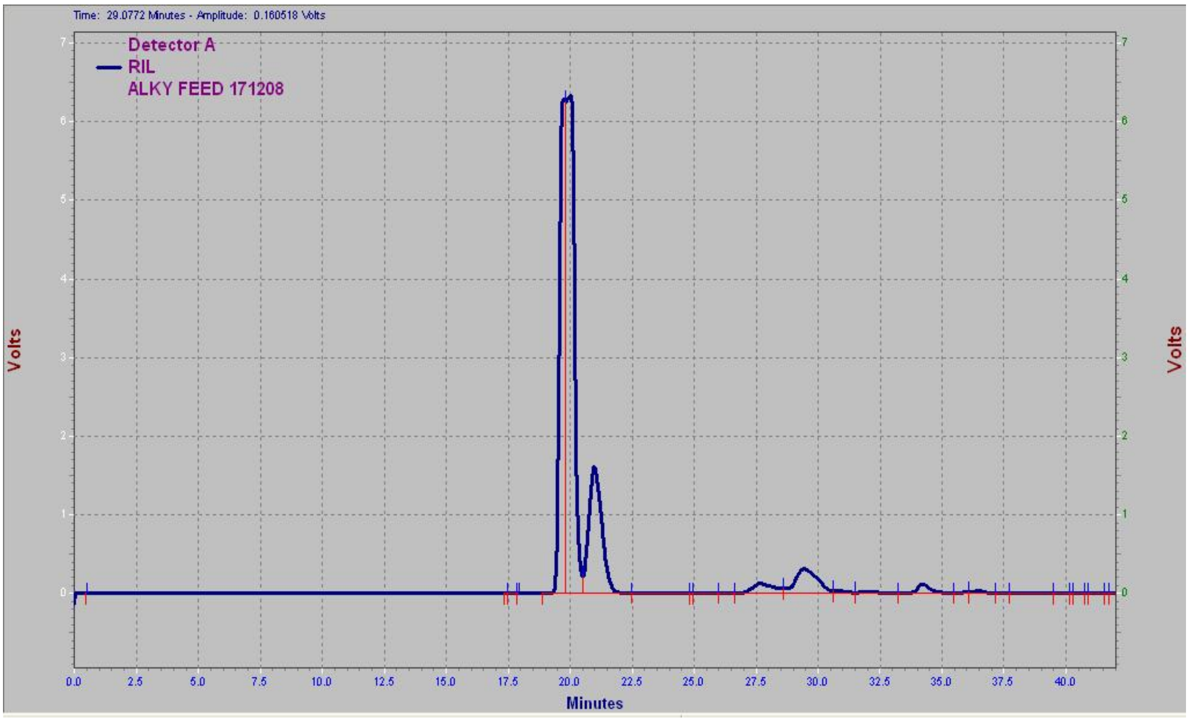
70. Dhanshri P. Sawant, S.B. Halligudi, *Alkylation of benzene with alpha-olefins over zirconia supported 12-silicotungstic acid*, Journal of Molecular Catalysis A: Chemical 237 (2005) 137-145.

71. Y. Cao, R. Kessas, C. Naccache, *Alkylation of benzene with dodecane. The activity and selectivity of zeolite type catalysts as a function of the porous structure*, Applied Catalysis A: General 184 (1999) 231-238.

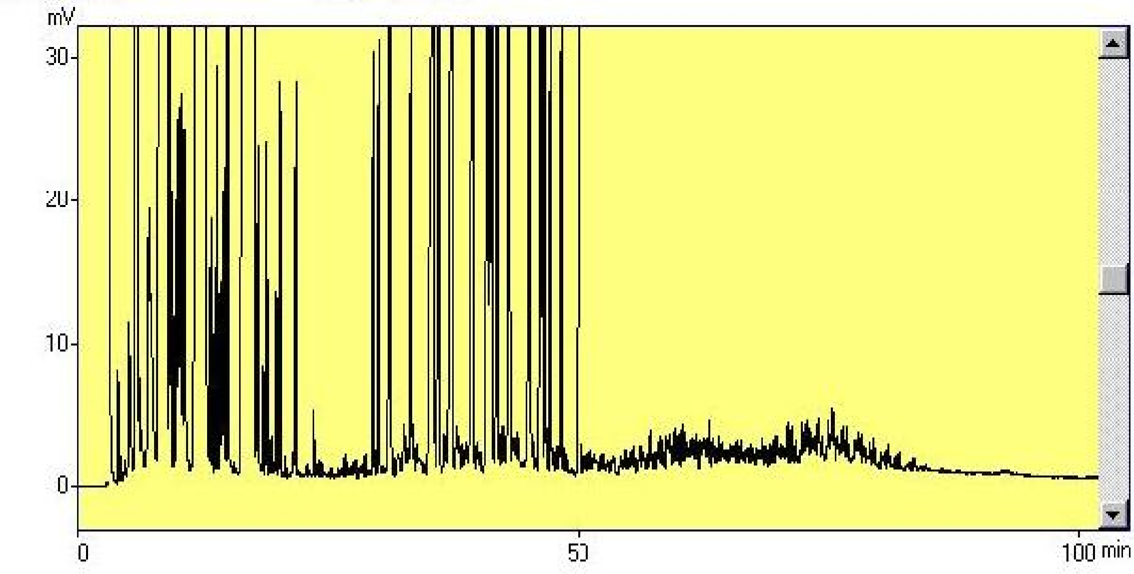
72. P.N. Borutskii, E.G. Kozlova, *Alkylation of benzene with higher olefins on heterogeneous catalysts*, Petroleum Chemistry, vol. 47,2007, pp 250-261.

Appendix A

Typical Feed Analysis Chromatogram by HPLC

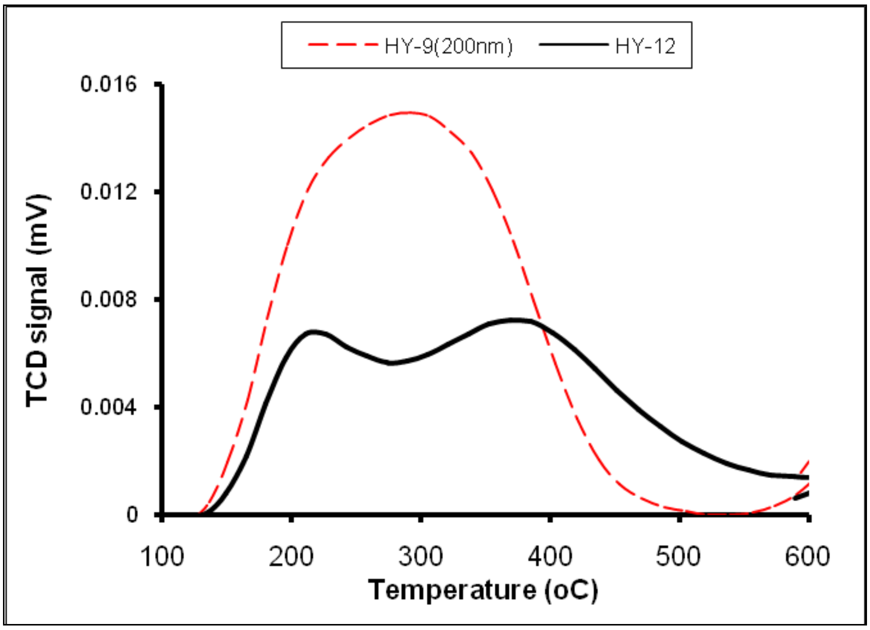


Typical Product Analysis Chromatogram by GC



Appendix B

Typical TPD analysis of zeolite catalysts



Appendix C

Calculation of Process Parameters of a Typical Run

Name of catalyst	HY-20		
Wt of Catalyst	5 gm		
BOR	10:1		
Temperature	100 °C		
Pressure	10kg/cm^2		
WHSV	1.5		
Feed	Benzene	+Decene +	Decane

S.No.	R.TIME	AREA	RF	CORR AREA	CONC
1	2.684	286	1	286	0.000865
2	2.789	665	1	665	0.002011
3	2.958	7241805	1	7241805	21.89599
4	3.853	399	1	399	0.001206
5	4.188	71597	1	71597	0.216477
6	4.658	962	1	962	0.002909
7	5.087	49454	1	49454	0.149527
8	6.37	21343275	1	21343275	64.53254
9	6.558	2729	1	2729	0.008251
10	6.648	3681	1	3681	0.01113
11	6.774	739	1	739	0.002234
12	6.85	1177	1	1177	0.003559
13	6.926	1107	1	1107	0.003347
14	6.99	778	1	778	0.002352
15	7.062	1394	1	1394	0.004215
16	7.213	1049	1	1049	0.003172
17	8.167	740210	1	740210	2.238065
18	8.267	176	1	176	0.000532
19	9.238	238	1	238	0.00072
20	9.637	245	1	245	0.000741
21	10.218	848	1	848	0.002564
22	10.52	725	1	725	0.002192
23	10.766	816	1	816	0.002467
24	10.952	2362	1	2362	0.007142
25	11.105	414	1	414	0.001252
26	11.306	33688	1	33688	0.101857
27	11.474	450	1	450	0.001361
28	13.891	439	1	439	0.001327

29	14.319	819	1	819	0.002476	
30	14.483	132	1	132	0.000399	
31	15.758	14481	1	14481	0.043784	
32	18.44	651	1	651	0.001968	
33	19.111	1597	1	1597	0.004829	
34	20.883	1146	1	1146	0.003465	
35	21.02	2774	1	2774	0.008387	
36	24.669	862	1	862	0.002606	
37	25.406	3817	1	3817	0.011541	
38	25.696	3228	1	3228	0.00976	
39	25.98	7666	1	7666	0.023179	
40	26.117	2745	1	2745	0.0083	
41	26.476	8003	1	8003	0.024198	
42	26.829	3815	1	3815	0.011535	
43	27.147	7639	1	7639	0.023097	
44	27.383	11653	1	11653	0.035233	
45	27.787	14110	1	14110	0.042662	
46	28.327	19624	1	19624	0.059334	
47	28.664	12623	1	12623	0.038166	
48	29.395	522223	1	522223	1.578969	LL-10-5
49	29.554	137817	1	137817	0.416697	LL-10-5
50	30.165	687312	1	687312	2.078125	LL-10-4
51	30.284	1255	1	1255	0.003795	NN-LAB
52	30.52	27641	1	27641	0.083574	NN-LAB
53	31.325	866593	1	866593	2.620191	LL-10-3
54	31.581	2161	1	2161	0.006534	NN-LAB
55	33.47	932590	1	932590	2.819736	LL-10-2
56	36.468	1116	1	1116	0.003374	
57	36.763	406	1	406	0.001228	
58	37.059	331	1	331	0.001001	
59	39.796	2034	1	2034	0.00615	
60	40.08	972	1	972	0.002939	
61	40.337	871	1	871	0.002634	
62	40.992	859	1	859	0.002597	
63	42.193	1051	1	1051	0.003178	
64	44.256	1181	1	1181	0.003571	
65	50.038	233	1	233	0.000704	
66	60.756	373	1	373	0.001128	
67	60.9	172	1	172	0.00052	
68	61.092	271	1	271	0.000819	
69	61.242	412	1	412	0.001246	
70	61.478	493	1	493	0.001491	
71	61.616	1205	1	1205	0.003643	
72	61.951	2489	1	2489	0.007526	
73	62.288	2291	1	2291	0.006927	
74	62.56	1469	1	1469	0.004442	
75	62.726	525	1	525	0.001587	
76	63.037	5496	1	5496	0.016617	
77	63.419	11060	1	11060	0.033441	
78	63.812	11424	1	11424	0.034541	
79	63.942	890	1	890	0.002691	

80	64.179	6811	1	6811	0.020593
81	64.421	4850	1	4850	0.014664
82	64.553	11207	1	11207	0.033885
83	64.897	27698	1	27698	0.083746
84	65.241	17200	1	17200	0.052005
85	65.536	1312	1	1312	0.003967
86	65.683	1194	1	1194	0.00361
87	65.914	19924	1	19924	0.060241
88	66.222	16513	1	16513	0.049928
89	66.516	19327	1	19327	0.058436
90	66.667	308	1	308	0.000931
91	66.897	21792	1	21792	0.065889
92	67.441	11950	1	11950	0.036131
93	67.632	3332	1	3332	0.010074
94	67.845	38095	1	38095	0.115182
95	68.278	624	1	624	0.001887
96	68.393	442	1	442	0.001336
97	68.908	302	1	302	0.000913
98	69.363	23378	1	23378	0.070685
99	71.108	513	1	513	0.001551
100	71.292	334	1	334	0.00101
101	71.483	201	1	201	0.000608
102	72.481	518	1	518	0.001566
103	76.406	611	1	611	0.001847
104	80.074	588	1	588	0.001778
105	83.554	328	1	328	0.000992

Under above operating condition we analysed the product composition by GC. Based on these results we were calculating other process parameter (in wt %) as follows:

Benzene = 21.89

LAB = 1.578969+0.416697+2.078125+0.003795+0.083574+2.620191+0.006534+2.819736

LAB = 9.6076

HA = Sum(Conc 56: Conc 105)

HA = 0.8107

Paraffin = 100 – (Benzene + LAB + HA)

Paraffin = 67.6856

Total Long Linear = 1.578969+0.416697+2.078125+2.620191+2.819736

Total long Linear Isomers = 9.5137

Total 2-phenyl isomer = 2.819736

2-pheny content = (Total 2-phenyl isomer/ Total long Linear) * 100

2-pheny content = 29.368 %

Total Non Normal Isomers = 0.003795 + 0.083574 + 0.006534

Total Non Normal Isomers = 0.0939

Non Normal content = Total NonNormal Isomers / (Total NonNormal Isomers+Total long Linear isomer)

Non Normal content = 0.0097 %

Linearity = (1 - (Non Normal content)) * 100

Linearity = 99.02 %

HA/LAB = (HA)/(HA +Total long Linear Isomers+ Total Non Normal Isomers) * 100

HA/LAB = 7.782 %