Mechanistic Studies on Dimerization of Olefins and Subsequent Alkylation of Phenol

By

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DEPARTMENT OF CHEMICAL ENGINEERING

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Mechanistic Studies on Dimerization of Olefins and Subsequent Alkylation of Phenol

A

Project Report

Submitted in partial fulfillment of the requirements

For the Degree of

Master of Technology in Chemical Engineering

(Chemical Process And Plant Design)

By

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May 2014

Declaration

This is to certify that

1. The thesis comprises my original work towards the degree of Master of Technology in Chemical Engineering (Chemical Process And Plant Design) at Institute of Technology, Nirma University and has not been submitted elsewhere for a degree.
2. Due acknowledgment has been made in the text to all other material used.

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Undertaking for Originality of the Work

I Shakti Bhardwaj, 12MCHC25, give undertaking that the major project entitled "**Mechanistic Studies on Dimerization of Olefins and Subsequent Alkylation of Phenol**" submitted by me, towards the partial fulfillment of the requirements for the degree of Master of Technology in Chemical Engineering (Chemical process and plant design) of Nirma University, Ahmedabad is the original work carried out by me and I give assurance that no attempt of plagiarism had been made. Due acknowledgement has been made in the text to all other material used.

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Acknowledgment

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Abstract

Production of less toxic alkylphenol ethoxylates, a subset of the family of non-ionic surfactants has been a topic of extensive research since adverse effects of detergent toxicology have been seen on aquatic life and their propagation in entire food cycle through means of water, soil and air has been observed, this led to ban on various non-ionic surfactants in several countries. When alkylphenol ethoxylate waste enters the environment it metabolizes into lower ethoxylated alkylphenols or alkylphenols at the end of anaerobic/ aerobic digestion. These lower metabolities are found to mimic the hormone oestradiol in fishes, birds and mammals.

In the present study attempts are made to produce alkylphenols with modified the structure. Dimers of olefins viz. 1-Octene, 2-Octene, 1-Decene, 2-Heptene and Dodecene are produced to alkylate phenol. At industrial level linear olefins are also found in cracked refinery streams having 6-24 carbon atoms, these are oligomerized by contacting with activated Y-zeolites. Detailed characterization of various grades of cationic zeolite catalyst is done for the selection of the optimum catalyst for obtaining high dimer yield and selectivity. Reaction operating parameters viz. temperature of the reaction, moisture content of the reactant, amount of catalyst used and duration of the reaction are also varied to find out the best operating conditions for all the reactions. Kinetics study is performed for all the reactions and the data obtained from the study has been used to fit to various rate equations which gives important information about the mechanism of the reaction. ^{13}C NMR of the pure dimers and final alkylphenols is obtained in order to understand the product composition at atomic levels.

Zeolite CBV 720 is found to be the best catalyst for dimerization of olefins used in this work due to its ability to give high dimer yield along with ability to minimize formation of higher oligomers. Rate of dimerization of 2-Octene if found to be fastest among other olefins under same operating conditions, this behavior is explained through various experiments and studies while discussing the results. The^{13}C NMR study also give a brief insight of the ortho/para distribution in the final alkylphenols.

Keywords : Alkylphenol Ethoxylate, Non-ionic Surfactants, Alkylphenol, Olefin, Dimer, Zeolite CBV 720.

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Abbreviations

APE	Alkylphenol Ethoxylate
POE	Polyethoxylate
NPE	Nonylphenol Ethoxylate
OPE	Octylphenol Ethoxylate
NP	Nonylphenol
OP	Octylphenol
FY	Financial Year
TPA	Ton Per Annum
MEAS	Measurement of Solubility
AMS	Alpha-Methylstyrene
TPD	Temperature programmed desorption
MR	Macro-Reticular
O/P	Ortho/Para
Temp.	Temperature
Coeff.	Coefficient
Wt.	Weight
gm.	Gram(s)
hrs.	Hours

Chapter 1

Introduction

Alkyl phenol ethoxylates (APEs) are a subset of the general family of surfactants called nonionic surfactants. Since the mid 1940s, APEs have been used commercially for their surfactant ability. The term surfactant includes surface-active compounds characterized by their ability to concentrate at surfaces and form micelles in solution [1]. APEs contain two main molecular regions: the polyethoxylate (POE) chain is polar and thus hydrophilic and the alkyl phenol is the hydrophobic area. The hydrophilic nature of the ethoxylate is attributed to the hydration of the ether-linked oxygen atoms [2].

There is large number of regulations on alkyl phenol ethoxylates; however these regulations in most cases pertain to the European Union. APEs are used as industrial cleaners and other processing aids from here they enter wastewater and end up in sewage treatment plants. Some APE waste is transferred into the environment and metabolized into lower ethoxylated alkylphenols, which are considered endocrine disrupters[3]. APEs have been found in fish, river sediment, and other environmental samples through analytical techniques[1][4][5][6][7][8].

Market demand of ethylene oxide (EO) in India has shown an increase of approximately 16.5% after FY06 by reaching to 173,000 TPA till FY10. The largest application of EO is in manufacture of surface active agents (nonionic alkylphenol ethoxylates and detergent alcohol ethoxylates). Till FY16 EO derivative demand is expected to reach 241,000 TPA with a growth rate of 6-7 %. Till now there are no regulatory norms in India governing the use of NPE or other alkyl phenol based ethoxylates. Even in United states NPE based detergents are still being marketed [9].

Alkyl phenols, such as nonyl and octyl phenol have been classified as toxic to the environment, primarily because of the fact that they have structures that can mimic oestrogen. Keeping this in mind, we decided to develop an alkyl phenol product that will have more branching in the alkyl chain and thus will not be able to mimic oestrogen and thus reduced toxicity levels are also expected (see Table 1.1). In this work dimers of olefins viz.1-Octene, 2-Octene and 1-Decene have been developed and used to alkylate phenol to fulfill the purpose of producing highly branched alkylphenols. A comprehensive experimental data has been generated for every step during the synthesis of alkyl phenol having desired properties and right reactivity pattern.

Table 1.1: Toxicology data of Alkylphenols

	2-tert-Butylphenol	4-tert-Butylphenol	4-tert-Pentylphenol	4-tert-Octylphenol	Nonyl phenol	Dodecylphenol (branched)	2,4-Di-tert-butylphenol	2,6-Di-tert-butylphenol
Physicochemical properties								
Water solubility (mg/l)	700 (meas)	610 (meas)	37	19 (meas)	6 (meas)	1	12	4.11
Octanol-water partition coeff. (log K_{ow})	2.7-3.5	3.3	4.03	4.12	4.48	5.5	5.19	4.5
Persistence								
Biodegradation	Readily biodegradable	Readily biodegradable	Not readily biodegradable	Inherently biodegradable	Inherently biodegradable	Not readily biodegradable	Not readily biodegradable	Not readily biodegradable
Bioaccumulation								
Highest fish BCF value	188 (est)	120	531 (est)	634 (est)	1.28	9,440 (est)	~660 (est)	660
Toxicity								
Acute toxicity (mg/l)	2.4	3.4	1.7	0.013	0.085	0.093	1.8	0.076
Chronic toxicity (mg/l)	0.042 (est)	0.73	0.063	0.006	0.025	No data available	0.008 (est)	0.019 (est)

1.1 Scope of the project

The aim of this Project is to identify the product composition on taking mixture of olefins to their dimers and subsequently alkylating them with a phenol to identify the right reactivity pattern and structural properties of the final alkyl phenols.

1.2 Objectives

- To find out the best catalyst for dimerization of olefins.
- To check the effect of parameters like moisture content, temperature, amount of catalyst used and duration of reaction on the yield of dimer. -
- To analyze the yield of Dimer, selectivity and total conversion vs. Olefin (1-Decene, 1-Octene, 2-Octene, 1-Heptene, Dodecene).
- To alkylate phenol with dimers obtained after purification and separation from by product(s) and un-reacted reactant.
- To generate kinetics data for all reactions involved in the process.
- To obtain pure alkylphenols by separation of by-products and reactants and report the process conditions.
- Characterization of final alkylphenol and dimers as and when required.
- To fit the experimental data to kinetics equations representing the respective reactions.
- To conclude the best olefin, process parameters and catalysts for the alkylation of phenol based on the overall experimental data and desired detergency properties.

Chapter 2

Literature Survey

2.1 Alkylphenol Ethoxylates as non-ionic surfactants: Historical developments.

The uses of alkyl phenol ethoxylates cover a wide range of industries from cleaning systems to paints and coatings to agricultural chemicals. A summary of product uses of alkyl phenol ethoxylates is given in Table 2.1 [10].

Liu.et. al. [11] found that octylphenol ethoxylates (OPE) and nonylphenol ethoxylates (NPE) with the ethyleneoxide mole ratio of 9-12 are the most effective surfactants for the removal of polycyclic aromatic hydrocarbons from soil.

Aqueous laundry detergents can also use alkyl phenol ethoxylates. Schwarts[12] has described the use of a mixture of ethoxylateddodecylphenol and nonylphenol in the detergent for the machine washing of delicate cotton articles.

Merrill and wood [13] has described the use APEs in combination with an anionic surfactant for use in low-foaming powdered laundry detergents.

Harrison and Weller [14] havediscussed the use of APEs in liquid laundry detergents containing anionic and cationic surfactants. He found that these cleaners are not only good detergents but also have very effective microbiocidal properties due to the inclusion of the cationic surfactant.

APEs can also clean hard surfaces. Scarderaet. al. [15] has invented an emulsion cleaner to clean surfaces contaminated by chemical warfare agents. Alkyl phenol (6) ethoxylate is suggested to serve as an emulsifier for solvents that are used in this emulsion cleaner.

Fuggini and streit [16] has invented a hard surface cleaner that effectively removes dirt and grease, leaving a protective barrier to repel soil. The preferred composition includes 2% of polyoxyethylene nonylphenol.

Magyar [17] also includes polyoxyethyelene nonylphenol and octyl phenol among the possible ingredients in an automotive cleaner well suited to cleaning whitewall tires, vinyl tops, and fabric interiors.

Polyoxyethylene alkylphenols are also useful in industrial metal cleaners. Sturwold [18] has described their use in cleaners to remove grease, oil, dirt, scale, and metal fines from metals.

Table 2.1: Applications of Polyoxyethylene Alkylphenols.

Agriculture	*Cleaners*	*Paper*
Emulsifiers and wetters Herbicidal adjuvants Fruit washes	Household detergents Dry cleaning detergents Industrial hand cleaners Metal cleaners	Pulping Absorbent papers De-inking waste water Wet-felt washing Adhesives
Paint	*Dust Wetting*	*Textiles*
Emulsion polymerization of latexes Latex stabilization Pigment wetting and dispersion	Coal mines Ceramic industries foundries	Bleaching Desizing agents Wetting and rewetting agent Mineral oil and solvent emulsifier Scouring agent Carbonizing of wool

2.2 Environmental issues associated with alkylphenol ethoxylates: Biodegradability

A vast number of laboratory-based biodegradation studies have been performed on APEs with the degree of biodegradation ranging from zero [19] to 100% [20], depending on the test methods used and the duration of the experiments. It has been accepted generally that rates of biodegradation of nonylphenol ethoxylate and octylphenol ethoxylates are slower than those of non-ionic surfactants produced by linear hydrophobes, such as polyoxyethylene alcohols[21]. However, studies of environmental levels of alkylphenols as well as the degree of their removal from wastewater suggest that the biodegradation rates are sufficient enough to prevent accumulation in the aquatic environment [22].

Biodegradation of the polyoxyethylene alkylphenols can occur via either an aerobic or an anaerobic pathway. The aerobic pathway generates lower mole-weight ethoxylates, carboxylic acid, derivatives of both ethoxylate and hydrophobe chain [23][24] unspecified intermediate biodegradation products, and ultimate biodegradation products (water and carbon dioxide). The anaerobic pathway generates lower mole-weight ethoxylates, alkyl phenol, unspecified intermediate metabolites, and ultimately, carbon dioxide and methane. It is presumed that anaerobic digestion of the carboxylic acid intermediates may also produce alkyl phenol in the route to ultimate biodegradation [25]. It is also proposed that microbial metabolism usually starts by an attack on the ethoxylate chain, rather than on the ring or the hydrophobic chain (Ball et al. [26]; Ahel et al.[27]). The ethoxylate groups are progressively removed, either by ether cleavage, or by terminal alcohol oxidation followed by cleavage of the resulting carboxylic acid (see Figure 2.1). The major source of alkyl phenol in the environment is through anaerobic digestion of the parent surfactant and the subsequent biodegradation intermediates.

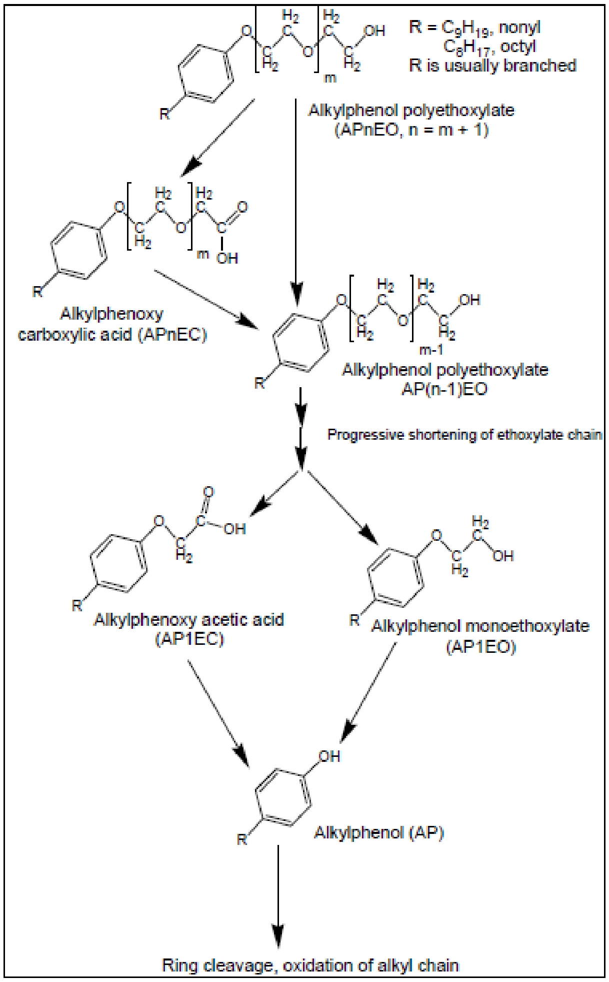


Figure 2.1: Microbial metabolism of alkylphenol ethoxylates.

2.3 Review on Alkylation of phenol

Basab Chaudhuri et. al. [28] have discussed the utility of various catalysts, such as Amberlyst 15, Amberlyst XN1010, and Nafion NR50, clay catalysts Filtrol 24 and Tonsil A/C, and homogeneous catalysts such as p-toluenesulfonic acid (p-TSA), in the mono-alkylation of phenol with α-methylstyrene (AMS) in the temperature range 60-120°C, and the ortho/para product distribution is compared. Both homogeneous and heterogeneous catalysts have been used for alkylation of phenol. Heterogeneous catalysts such as macroporous cation- exchange resins are preferred to homogeneous acid catalyst since they can easily be separated from the reactant-product mixture. The other major advantage of ion-exchange resin catalyst is that they eliminate undesirable side reactions and they eliminate corrosive environment that is often encountered with homogeneous catalysts.

It has been observed that in the alkylation of phenol with the olefins such as propylene and 1-butene which give secondary carbocations, the ortho alkylation is predominant even at elevated temperature. For Isobutylene and Isoamylene which give tertiary carbocations initially a high o/p ratio is obtained; which drops with an increase in temperature due to isomerization of ortho-alkylated product to para-alkylated product. The study concludes that the ion-exchange resin is shape selective and favours para-alkylation. Macroreticular cation-exchange resin Amberlyst 15 catalyst is found to be the most suitable catalyst among those studied, in the alkylation of phenol with AMS.

Curt B. Campbell et. al. [29] have proposed that Alkylation of phenol or catechol with olefins capable of forming tert-alkylcarbonium ions, catalyzed via sulfonated cation-exchange resin (Amberlyst-15), gives the corresponding tert-alkylphenols at 25-130°C, with higher temperatures favouring the para isomer. Alkylation at 140-150°C is unexpectedly found to give sec-alkylphenols, with both ortho and para isomers being formed in almost equal amounts. Low stability of tert-alkylphenols leads to reversibility of the alkylation reaction and subsequent formation of thermodynamically more stable sec-alkylphenols. The rearrangement of tert-alkylphenols to sec-alkylphenols is favoured when the tert-alkyl substituent is larger than tert-butyl.

Studies by (Baer et al. [30]; Billets et al. [31]) have shown that p-alkyl phenol isomer imparts improved performance properties to the class of metallic detergents used in lubricating oils, known as phenates and maximizing the 4-alkylcatechol isomer relative to 3-alkylcatechols overcomes toxicological problems associated with the biologically active 3-alkylcatechols.

The most pertinent examples in the literature on the reaction of phenolics with branched species are limited to C4 systems (olefins, alcohols, halides) and propylene oligomers (C9, C12). In the former examples, the tert-butylphenols produced do not isomerize into sec-butylphenols. In the latter examples, the products are extremely complex, and the sec-alkyl isomers are difficult to detect. To get insight into the novel rearrangement occurring during alkylation, the rearrangement of neat p-(2-methyl-2-undecyl) phenol is studied over commercial Amberlyst-15 catalyst. Higher operating temperature and longer reaction times favour the formation of sec- alkylphenols. Tert-alkylphenols are not stable at temperature above 140°C and undergoes dealkylation. Thus it can be expected that initially formed tert-alkylcarbonium ions will have time to equilibrate including the formation of sec-alkylcarbonium ions. Amberlyst-15 is a heterogeneous acid of only moderate acidity and the possibility of rearrangements of tert-alkyphenols has not been recognized until now, nor have the experimental conditions been reported.

Qisheng Ma. Et. al. [32] have developed a molecular level understanding of the mechanism of the phenol alkylation in the presence of a cation-exchange resin catalyst, Amberlyst-15. The catalyst is modelled with the benzene sulfonic acid, and the effect of this acid on olefins such as isopropene and tributene in a phenol solution mimics the experimental condition. A neutral-pathway mechanism is established to account for early-stage high concentration of the phenolic ether observed in experiments. The mechanism involves an exothermic reaction between olefin and the benzene sulfonic acid to form ester followed by three reaction pathways leading to direct O-alkylation, o-C-alkylation, and p-C-alkylation. Through calculations it has been concluded that O-alkylation to form the phenolic ether is the most energetically favourable in the neutral condition. An ionic rearrangement mechanism describes intramolecular migrations of the alkyl group from the phenolic ether to form C-alkylphenols, while the positively charged protonation significantly lowers transition barriers for these migrations. The ionic rearrangement mechanism accounts for high yields of o-C-alkyl phenol and p-C-alkyl phenol. Competition between the H atom and the alkyl R group at the substitutive site of the protonated ortho configuration is found to be the determining factor to the ortho/para ratio of C-alkylation products. The p-alkyl phenol isomer imparts improved performance properties to the class of metallic detergents used in lubricating oils, known as phenates.

2.4 Review on catalyst used for alkylation of phenol.

The technique generally used to synthesize alkylphenols is Friedel-Crafts alkylation. C3 to C12 alkylates are generally made through acid catalysis using sulphuric acid, BF3 or strong acid catalysts like Amberlyst 15 Dry, Amberlyst 35 Dry or Amberlyst 36 Dry. Specification sheet provided by manufacture for Amberlyst cation exchange resins is given in Table 2.2. Figure 2.2 shows the structure of amberyst catalyst.The choice of the Amberlyst catalyst depends very much on the type of alkene. Amberlyst polymer based catalysis involves mostly the use of functionalized styrene divinylbenzene copolymers with different surface properties and porosities. They are supplied as spherical polymers in the gel or macroreticular form. Besides their catalytic performance, amberlyst polymer catalysts are easy to handle and show a low degree of corro7sivity or organic fouling. Amberlyst 35 DRY and Amberlyst 36 DRY are the highest performing polymer based catalysts and represent the benchmark for phenol alkylation[33].

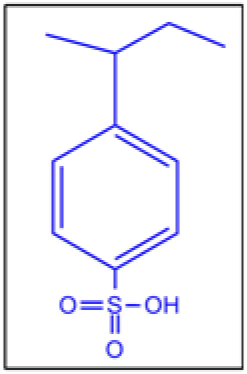


Figure 2.2: Structure of amberlyst catalyst.

Table 2.2: Amberlyst specification sheet provided by manufacturer.

Product name	Matrix	Functional groups	Capacity (Eq./kg)	Max. Op.Temp.	Remarks
Amberlyst 15 Dry	MR*	SO_3H	4.70	120	Standard grade resin**
Amberlyst 35 Dry	MR*	SO_3H	5.20	150	High temperature stability and excelletnt kinetics**
Amberlyst 36 Dry	MR*	SO_3H	5.40	150	Very high temperature stability**
*MR=Macroreticular, **For alkylation reactions					

Phenol reacts with branched olefin dimers, $C_{2n}H_{4n}$, including propylene tetramer, propylene trimer and diisobutylene, in presence of a dry macroporous strongly acidic catalyst at 120°C to 150 °C to give alkylphenols.

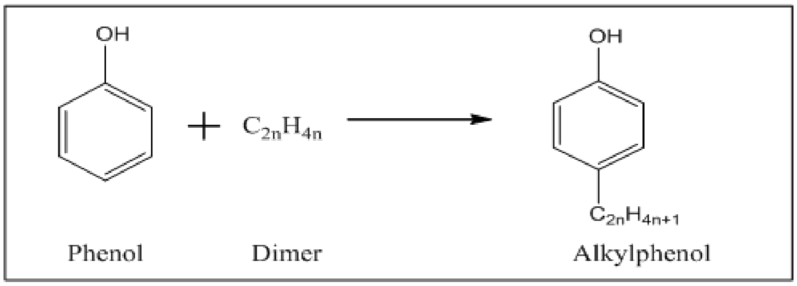


Figure 2.3: Alkylation of phenol through an olefin dimer.

Amberlyst dry catalysts have been especially designed for application in alkylation of phenol and have been dried to an optimal degree of moisture in order to ensure a high conversion rate and excellent selectivity. Their physical stability makes them well suited to stirred tank reactors and allows an extremely efficient separation from the reactants. Their optimized pore size distribution gives good diffusion rates and a long life. In this work Amberlyst 36 Dry is used to alkylate phenol with highly branched olefins. Typical specification of this catalyst is illustrated in table.

Table 2.3: Specification sheet: Amberlyst 36 Dry

Physical form	Opaque beads
Ionic form as shipped	Hydrogen
Concentration of acid sites	$\geqslant$5.40 eq/Kg
Water content	$\leqslant$1.65 %
Fines content	<0.300mm : 5.0% max
Coarse beads	>1.180mm : 5.0% max
Surface area	33 m^2/g
Average pore diameter	240 $\mathring{A}$
Maximum operating temp.	150 ^{o}C

2.5 Dimerization of linear olefins: Historical developments

The degree of the oligomerization is affected by the catalyst and reaction conditions employed during the reaction. The length of the carbon chain of the monomer starting material also has a direct influence on the properties of the oligomer products.

Initial known approach to oligomerize long chain olefins, generally having 10 carbon atoms, was to contact the olefin with boron trifluoride together with a promoter at a reaction temperature sufficient to effect oligomerization of the olefin [34][35][36]. However, boron trifluoride was found to be a pulmonary irritant, and breathing the gaseous fumes formed by hydration of the gas with atmospheric moisture has possessed health hazards. Thus, a method for oligomerizing long chain olefins using a less hazardous catalyst was the need of the hour.

Developments in zeolites and their application as catalysts to oligomerize lower olefins to gasoline, jet fuel and diesel have been reported [37]. Many reports suggest contacting long carbon chain olefins with acidic clays, zeolites and chemically activated zeolites to form oligomers. The long chain alpha-olefins suitable for oligomerization are generally made by the thermal cracking of paraffinic hydrocarbons or by the well-known zeigler ethylene chain growth and displacement process using triethyl aluminium.

Texaco discovered that it was possible to oligomerize long chain olefins using certain acidic montmorillonite clay catalysts [38]. They also discovered that synthetic lubricant base stocks can be prepared by oligomerizing linear olefins using a sulfate activated Group IV oxide, particularly zirconium dioxide [39]. An improved process was also disclosed by Texaco for oligomerizing linear olefins using a catalyst comprising a super-dealuminated Y-zeolite.

Intermediate pore size silicaceous crystalline molecular sieves were used to oligomerise olefins at elevated temperature with lower hydrogen transfer activity [40]. A patent assigned to Mobil Oil Corporation[41] describes the conversion of lower olefins to $C_{10}+$ distillate range by use of large pore crystalline aluminosilicate zeolite catalysts at elevated temperatures and pressures.

It has been discovered that a conversion of long chain olefins to oligomer may be effected by contacting the paraffins/olefins petroleum fraction, obtained from the cracked refinery distillate stream, with a catalyst comprising a Y-zeolite. The extent of oligomerisation of these olefins is found to be appreciably enhanced when the Y-zeolites had higher silica/alumina ratio, i.e., super-dealuminated ultrastable Y-zeolites. In addition to being excellent catalysts, these Y-zeolites and super-dealuminated ultrastable Y-zeolites are found relatively safe and are more easily handled than boron trifluoride. The suitable commercially available catalysts of super-dealuminated category include CBV 712, CBV 720, CBV 760 and CBV 780 and having a silica to alumina ratio in the range of 10:1 to 80:1. These catalysts which are generally available in powdered form can be easily made in pellets, or extrudates with the help of certain binders, which could be of silica alumina type. These extrudated Y-catalysts had required physical stability and strength necessary for performing the catalytic reactions on a fixed bed reactor. However, for oligomerisation reactions to be done in autoclave (slurry reactor), the commercially available powdered catalysts as such can be used [42].

2.6 Mechanism of the reactions

The formation of linear olefin dimers is the result of head to head coupling of alpha olefins. Starting from a metal hydride active species, the first step is a (1,2) insertion of an alpha olefin to generate a primary alkyl species. It is followed by a (2,1) insertion of the olefin in the metal alkyl bond then linear dimers isomers are formed by chain transfer (Beta-H elimination to metal or Beta-H transfer to monomer). There is no catalyst known to produce only linear dimers from alpha olefins. For the best catalytic systems, the selectivity into linear dimers in the dimer fraction was generally less than 80% and these systems based on non ionic nickel complexes containing chelating ligands like acetylacetonate generally exhibit low activity (see Figure 2.4).

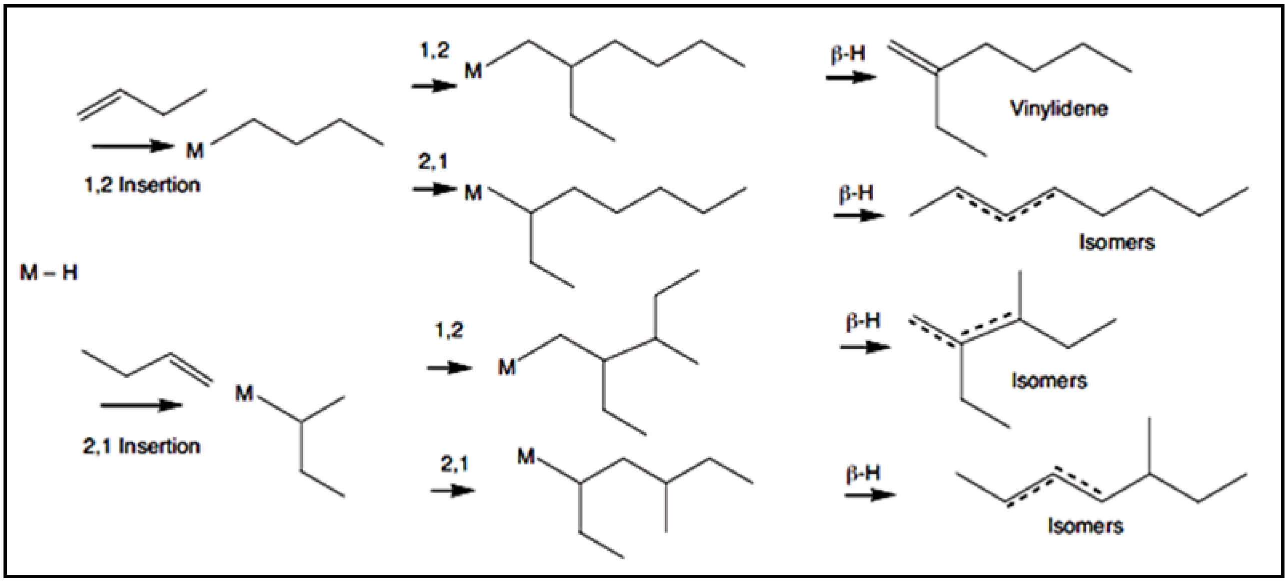


Figure 2.4: Reaction Pathway 1 - Butene Dimerization

The generally accepted mechanism in a typical non-selective ethylene oligomerization process is a Cossee-Arlman-type mechanism featuring successive olefin insertion steps followed by Beta-H elimination to generate this distribution of Alpha- olefins. Two molecules of ethylene coordinate to chromium, which then undergoes oxidative coupling, generating a chromacyclopentane. The transition state for Beta-H elimination from the chromacyclopentane leading to1-butene is geometrically too strained to allow facile Beta-H elimination, which is depicted by the minimal yield of 1-butene observed. A third molecule of ethylene coordinates and subsequently inserts into the Cr-C bond to generate a chromacycloheptane. From the chromacycloheptane, release of 1-hexene is fast, preventing further ring growth and thus formation of higher Alpha-olefins (see Figure 2.5)[43].

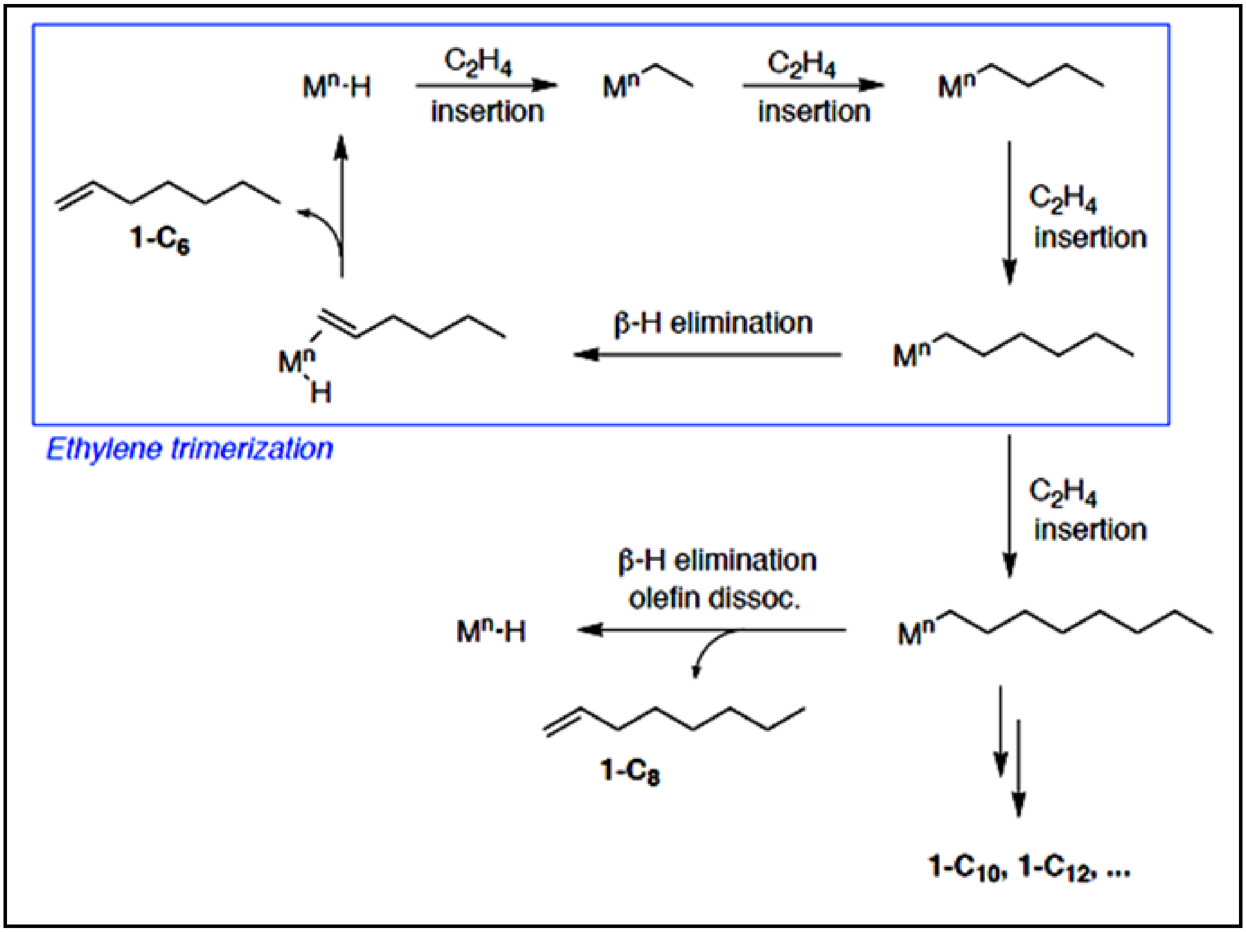


Figure 2.5: Mechanism during generic ethylene oligomerization

An ionic rearrangement mechanism describes intra-molecular migrations of the alkyl group from the phenolic ether to form C-alkylphenols, while the positively charged protonation significantly lowers transition barriers for these migrations. The ionic rearrangement mechanism accounts for high yields of o-C-alkyl phenol and p-C-alkyl phenol. Competition between the H atom and the alkyl R group at the substitutive site of the protonated ortho configuration is found to be the determining factor to the ortho/para ratio of C-alkylation products. Five possible protonated configurations (p-ether, p-ipso, p-ortho, p-meta and p-para) are shown and the migration paths of the alkyl group (R) from the p-ether to p-para configurations are also illustrated in Figure 2.6[32].

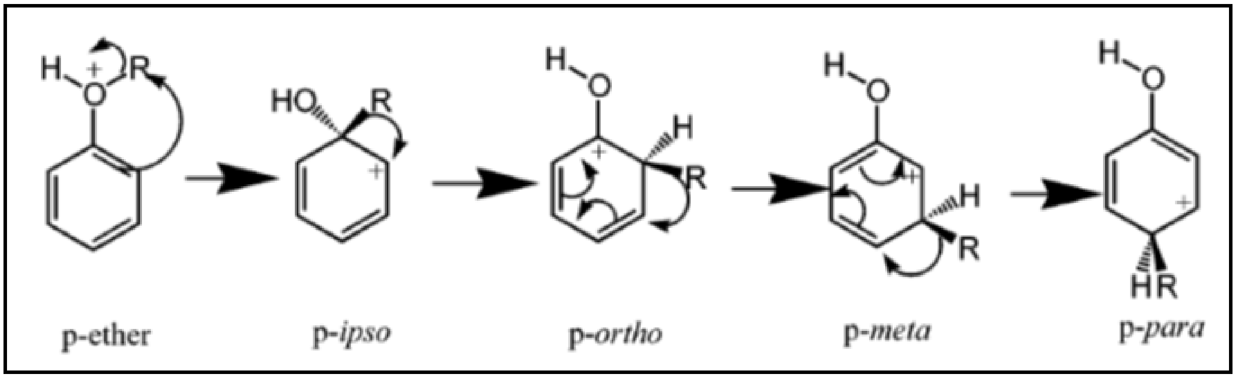
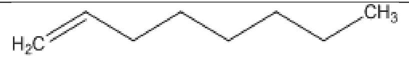
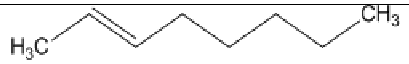
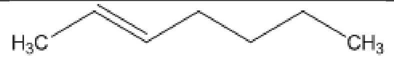
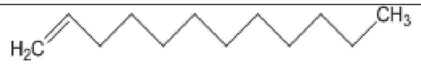


Figure 2.6: Five possible protonated configurations, p-ether, p-ipso, p-ortho, p-meta, and p-para, for migration of the alkyl in the ionic pathway

2.7 Properties of olefins used in the present study

Following are the oefins use in the study for dimerizationa and subsequent alkyaltion of phenol. None of these olefin pose any serious health hazard on inhalation ans touch to the skin. Although their direct intake by any means is prohibited. All are liquid at room temperature and do not come in the category of extremely flamable substances.

Table 2.4: Physical and chemical properties of olefins.

Name	Molecular formula	Structure	Boiling point (°C)	Molar mass (g/mol)
1-Octene	C_8H_{16}		121	112.24
2-Octene	C_8H_{16}		123	112.24
1-Decene	$C_{10}H_{20}$		172	140.27
2-Heptene	C_7H_{14}		94	98.18
Dodecene	$C_{12}H_{24}$		213.8	168.31

Chapter 3

Experimental section

Aim of this work is to first produce dimers of various olefins and subsequently produce alkyl phenols by using dimers as the alkylating agents and to experimentally determine the most suitable process parameters for the dimerization and then alkylation of phenol. The Dimers of Olefins viz. 1-octene, 2-octene, decene, heptene and dodecene are produced, purified and subsequently alkylation of phenol has been carried out with a few of these dimers, reaction kinetics has been studied throughout the process.

3.1 Catalyst characterization for Dimerization reaction

It has been reported several times in literature that zeolites with a high Sio_2/Al_2O_3 mole ratio are the most ideal catalysts for dimerization of olefins [patents]. Owing to their structural and chemical properties zeolites are found to give high yields and good selectivity for the dimers only. The pore size distribution and pore volume of these catalysts is found to selectively allow only dimeric structures to pass through them as products thereby avoiding the formation of higher oligomers. Formation of higher oligomers in a dimerization reaction is very undesirable due to difficult separation from the respective dimers and loss of catalyst activity due to their entrapment inside the active sites or pores.

Zeolite catalysts of specifications mentioned in table 3.1 have been extensively studied to find out the best among these to be used for the dimerization of olefins. Surface Characteristics, site acidity and the yield of dimer obtained in dimerization reactions is recorded; by the use of this data, the most suitable catalyst for the dimerization of olefin is found. The desired catalyst must have good selectivity and yield of dimer, must not decompose at high reaction temperatures, must have optimum acidity required by the reactants and must possess high regenerability. As discussed earlier that dimerization reaction precedes in an acidic environment so the catalysts with hydrogen as nominal cation has been used for the reactions. A comparative data set is also generated for a reaction performed with an ammonium cation form catalyst CBV 712. Later this catalyst is heated at 560 °C for 4 hours in a closed furnace; this process turns NH^{4+} cation into H^+ cationic form through the loss of NH_3 at high temperatures. Thus, reactivity pattern for the transformed catalyst is also recorded.

Table 3.1: Catalyst Specification sheet provided by manufacturer

Zeolyst Products	SiO_2/Al_2O_3 Mole Ratio	Nominal Cation Form	Na_2O weight %	Unit cell size (Å)	Surface Area (m^2/g)
CBV 600	5.2	Hydrogen	0.2	24.35	660
CBV 712	12	Ammonium	0.05	24.35	730
CBV 720	30	Hydrogen	0.03	24.28	780
CBV 780	80	Hydrogen	0.03	24.24	780

3.1.1 Reaction behaviour study with various grades of zeolites

Dimerization of 1-octene is done with the catalysts CBV 600, CBV 712 (NH_3cation), CBV 712 (H cation), CBV 720 and CBV 780. Temperature of the reaction is 125°C and amount of catalyst used is 1.5 gram catalyst for every 10 gram of reactant. 6 hour reaction kinetics is recorded by analyzing reaction samples in GC at pre-defined time intervals. The Total conversion, Dimer yield and Trimer yield are calculated separately as follows:

$$Total\ Conversion = \frac{Area(Dimer + Trimer) \times 100}{Area(Reactant + Dimer + Trimer)} \tag{3.1}$$

$$Dimer\ Conversion = \frac{Area(Dimer) \times 100}{Area(Reactant + Dimer + Trimer)} \tag{3.2}$$

$$Trimer\ Conversion = \frac{Area(Trimer) \times 100}{Area(Reactant + Dimer + Trimer)} \tag{3.3}$$

Unconverted Reactant Calculation:

1. Take several standard samples of Reactant and diluent keeping weight of diluents as constant and changing weight of reactant for every sample.
2. Do the GC analysis for all samples, record the respective peak areas.
3. Find:

$$Peak\ Area\ Ratio = \frac{Area\ of\ reactant}{Area\ of\ diluent} \tag{3.4}$$

$$Weight\ ratio = \frac{Weight\ of\ reactant\ in\ the\ sample}{Weight\ of\ diluents\ in\ the\ sample} \tag{3.5}$$

4. Use these ratios to form a plot, this must result in a linear plot following the equation y = mx + c, slope 'm' denotes the response factor.
5. Perform reaction, take diluted reaction samples, perform GC and calculate the Peak area ratio and weight ratio in the similar way as discussed in step 3. The weight ratio is the 'Obtained Weight Ratio' now.

6. Expected weight ratio also known as theoretical weight ratio is calculated as follows:

$$Expected\,Weight\ Ratio = m \times Peak\ Area\ Ratio \tag{3.6}$$

7. The unconverted reactant is calculated as a ratio of the two weight ratios obtained above:

$$\%\,Unconverted\,reactant = \frac{Expected\,Weight\ Ratio \times 100}{Obtained\,Weight\ Ratio} \tag{3.7}$$

Table 3.2: Standard Sample data for 1-Octene.

Octene Wt. (gm.)	Hexane Wt. (gm.)	Wt. Ratio (R1)	Peak Area Ratio (R2)	z = R1/R2
0.04	0.15	0.24	0.30	0.80
0.06	0.15	0.38	0.46	0.82
0.07	0.15	0.45	0.56	0.81
0.08	0.15	0.48	0.59	0.82
0.11	0.15	0.70	0.77	0.90

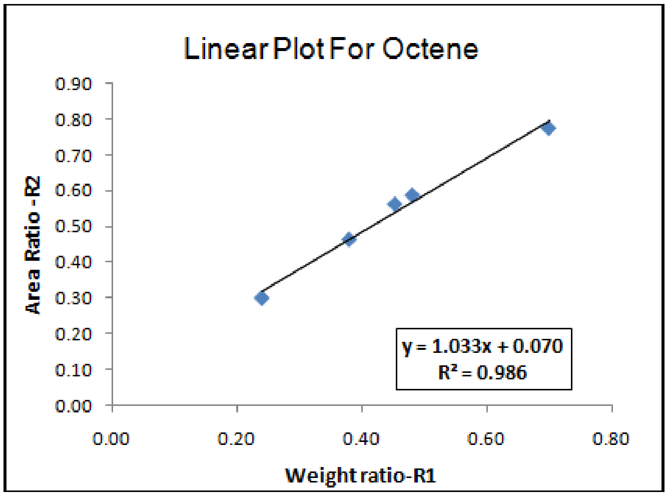


Figure 3.1: Linear plot for 1-Octene.

Table 3.3: Standard Sample data for 1-Decene.

Octane Wt. (gm.)	Hexane Wt. (gm.)	Wt. Ratio (R1)	Peak Area Ratio (R2)	Z = R1/R2
0.05	0.15	0.34	0.55	0.63
0.03	0.15	0.22	0.34	0.64
0.05	0.15	0.33	0.55	0.59
0.07	0.17	0.42	0.70	0.60
0.11	0.15	0.70	0.77	0.90

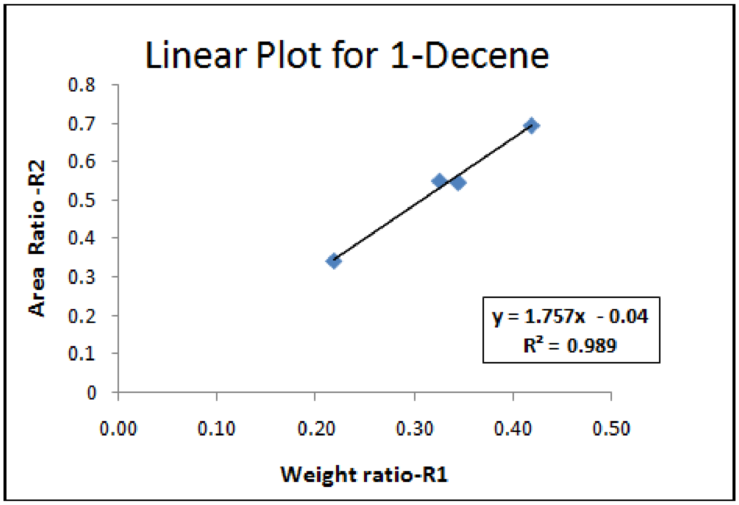


Figure 3.2: Linear plot for 1-Decene.

The experiments are performed in Radley Reactor. This reactor contains 6 slots for the reaction in 100 ml/250 ml round bottom flasks. Temperature and RPM of the reactor are adjustable. The top of radley's flasks is equipped with a 15 cm long glass condenser section which facilitates reflux of vapor formed during the reaction. The gas chromatogram used for analysis isRestek madeGC Rtx-1equipped with an FID detector, fitted with a 30 meter capillary column of 0.53 mm i.d. and 0.25 µm df. It can withstand a maximum program temperature of 340°C with a minimum bleed temperature of 320°C.

Figure 3.3: Radley Reactor Setup.

3.1.1.1 Reaction behaviour study with CBV 600.

The catalyst CBV 600 is kept for activation in a closed furnace at 350 °C for 4 hrs. It is stored and sealed with parafilm for one day. Reaction is set up in Radleyreactor attemperature 125°C and fixed agitation speed of 550 rpm.

Table 3.4: Dimerization reaction kinetics study of 1-Octene with CBV-600 catalyst.

Time (hrs.)	Conversion (%)	Dimer yield (%)	Trimer yield (%)	Un-converted 1-Octene, %
0.25	3.7	3.5	0.19	87.4
0.5	3.2	3.0	0.20	82.0
0.75	5.1	4.8	0.26	77.1
1.0	5.0	4.7	0.32	75.0
1.5	5.5	5.6	0.29	69.4
2.0	5.3	5.5	0.15	65.0
2.5	5.0	4.7	0.25	68.0
3.0	6.6	6.2	0.40	67.4
4.0	7.1	6.7	0.37	65.6
5.0	6.6	6.2	0.36	67.6
6.0	7.2	6.7	0.48	60.3

Maximum conversion reached by the reaction is 7.2 % in which 6.7 % is dimer and only 0.48 % trimer is found. The reaction proceeds at a slow rate, selectivity of the catalyst is observed to be good but very less dimer yield is obtained. Figure 3.4 shows the trend of plot obtained with the kinetics data.

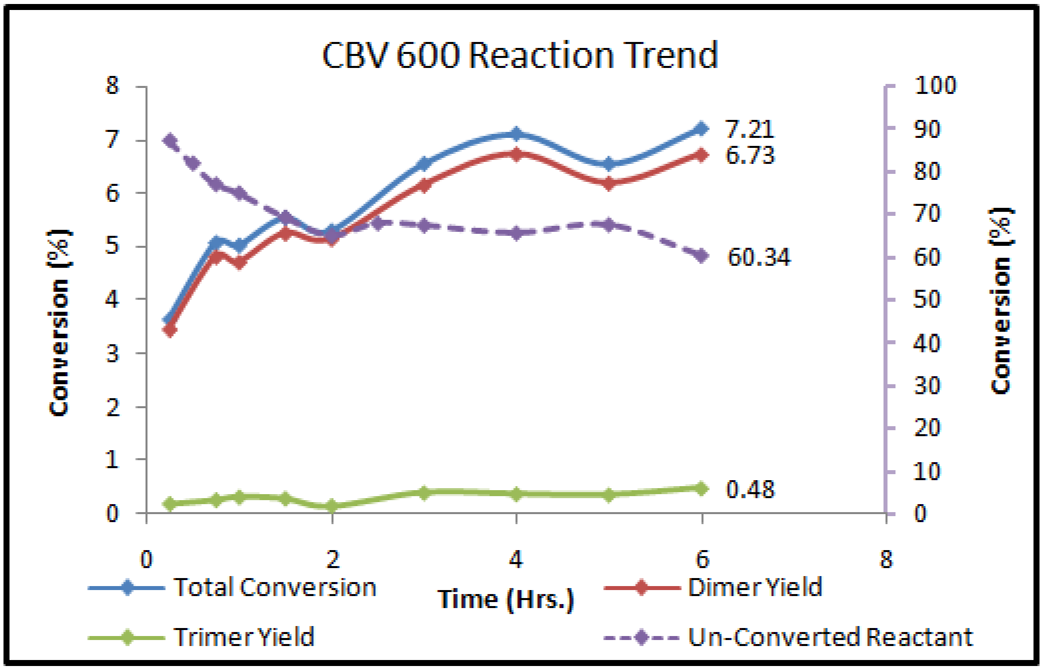


Figure 3.4: Plot showing % conversion vs. Time for dimerization reaction of 1-Octene with the catalyst-zeolyst CBV600.

3.1.1.2 Reaction behaviour study with CBV 712 (NH_3 Cation).

The catalyst CBV 712 is kept for activation in a closed furnace at 350 °C for 4 hrs. It is stored and sealed with parafilm for one day. Reaction is set up in Radley's reactor at temperature 125°C and fixed agitation speed of 550 rpm.

Table 3.5: Dimerization reaction kinetics study of 1-Octene with CBV 712 (NH_3Cation)

Time (hrs.)	Conversion (%)	Dimer yield (%)	Trimer yield (%)	Un-converted 1-Octene, (%)
0.25	4.9	0.29	0.29	82.1
0.5	6.5	6.1	0.37	74.5
0.75	5.8	5.4	0.42	74.5
1.0	5.2	4.9	0.29	71.6
1.5	5.4	5.2	0.28	72.7
2.0	6.5	6.3	0.27	74.3
2.5	6.2	5.7	0.45	68.6
3.0	8.9	8.3	0.68	69.8
4.0	7.9	7.4	0.46	70.2
5.0	7.7	7.2	0.50	64.7
6.0	9.7	9.0	0.65	64.9

Maximum conversion reached by the reaction is 9.7 % in which 9% is dimer and only 0.65 % trimer is found. The reaction proceeds at a slow rate, selectivity of the catalyst is observed to be good but very less dimer yield is obtained. Figure 3.5 shows the trend of plot obtained with the kinetics data.

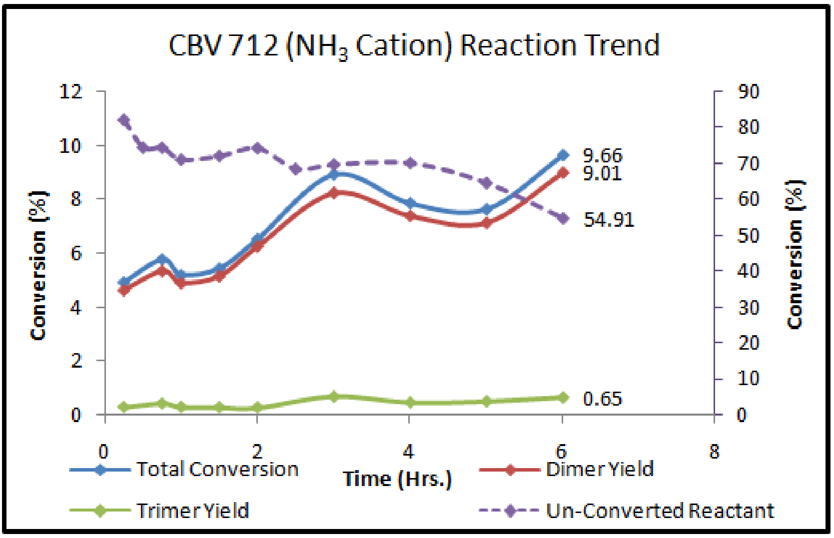


Figure 3.5: Plot showing % conversion vs. Time for dimerization reaction of 1-Octene with the catalyst-zeolyst CBV 712 (NH_3Cation).

3.1.1.3 Reaction behaviour study with CBV 712 (H Cation).

The catalyst CBV 712 is kept for activation in a closed furnace at 560°C for 4 hrs. It is stored and sealed with parafilm for one day. Reaction is set up in Radley's reactor at temperature 125°C and fixed agitation speed of 550 rpm.

Table 3.6: Dimerization reaction kinetics study of 1-Octene with CBV 712 (H-Cation)

Time (hrs.)	Conversion (%)	Dimer yield (%)	Trimer yield (%)	Un-converted 1-Octene, (%)
0.25	6.3	5.8	0.47	52.5
0.5	5.9	5.5	0.38	52.3
1.0	12.7	11.7	0.95	48.3
1.5	11.5	10.7	0.76	47.3
2.0	13.0	12.0	1.1	45.3
2.5	20.3	18.7	1.6	41.0
3.0	17.7	16.5	1.2	38.8
4.0	20.7	19.3	1.5	37.9
5.0	23.0	21.1	1.9	35.6
6.0	31.7	29.4	2.3	33.4

Maximum conversion reached by the reaction is 31.7 % in which 29.4 % is dimer and only 2.3 % trimer is found. The reaction proceeds at a good rate, selectivity of the catalyst is observed to be good and an appreciable amount of dimer is obtained. Figure 3.6 shows the trend of plot obtained with the kinetics data.

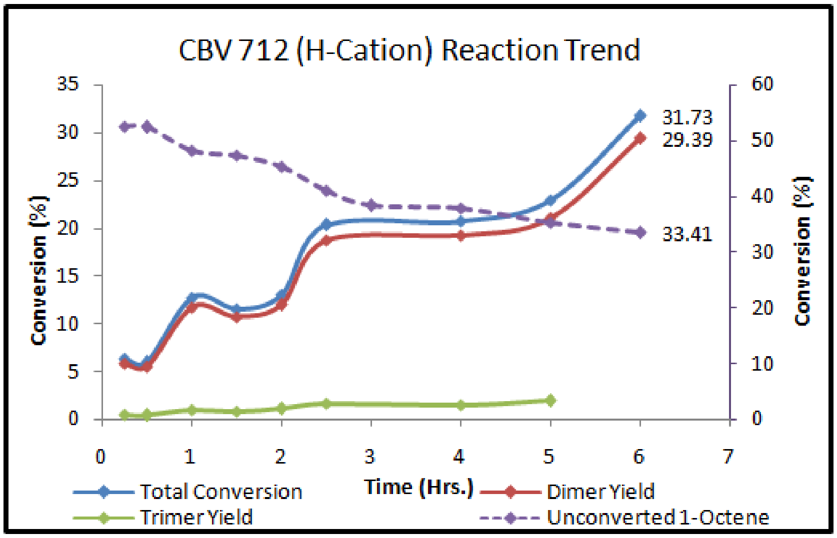


Figure 3.6: Plot showing % conversion vs. Time for dimerization reaction of 1-Octene with the catalyst-zeolyst CBV 712 (H Cation).

3.1.1.4 Reaction behaviour study withCBV 720

The catalyst CBV 720 is kept for activation in a closed furnace at 350 °C for 4 hrs. It is stored and sealed with parafilm for one day. Reaction is set up in Radley's reactor at temperature 125°C and fixed agitation speed of 550 rpm.

Table 3.7: Dimerization reaction kinetics study of 1-Octene with CBV 720

Time (hrs.)	Conversion (%)	Dimer yield (%)	Trimer yield (%)	Higher Oligomer, (%)	Un-converted 1-Octene, (%)
0.25	20.1	18.4	1.7	–	56.2
0.5	19.5	18.1	1.5	0.08	42.4
0.75	34.6	31.2	3.5	0.11	42.8
1.0	33.4	30.4	3.0	–	38.7
1.5	43.4	38.8	4.7	0.29	38.0
2.0	46.2	40.7	5.5	0.32	28.0
2.5	39.8	35.4	4.4	0.25	29.1
3.0	44.1	38.6	5.5	0.50	27.6
4.0	46.2	41.3	5.0	0.32	25.5
5.0	46.3	39.1	7.2	0.65	26.5
6.0	61.2	52.5	8.7	0.53	24.3

Maximum conversion reached by the reaction is 61.2 % in which 52.5 % is dimer and only 8.7 % trimer is found. The reaction proceeds at a good rate, selectivity of the catalyst is observed to be good and an appreciable amount of dimer is obtained. Figure 3.7 shows the trend of plot obtained with the kinetics data.

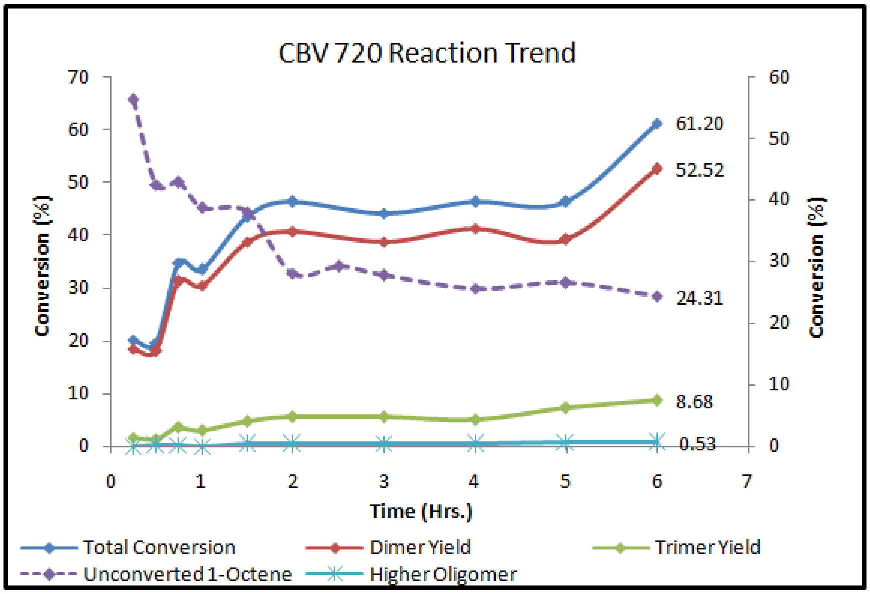


Figure 3.7: Plot showing % conversion vs. Time for dimerization reaction of 1-Octene with the catalyst-zeolyst CBV 720.

3.1.1.5 Reaction behaviour study with CBV 780

The catalyst CBV 780 is kept for activation in a closed furnace at 350 °C for 4 hrs. It is stored and sealed with parafilm for one day. Reaction is set up in Radley's reactor at temperature 125°C and fixed agitation speed of 550 rpm.

Table 3.8: Dimerization reaction kinetics study of 1-Octene with CBV 780

Time (hrs.)	Conversion (%)	Dimer yield (%)	Trimer yield (%)	Higher Oligomer, (%)	Un-converted 1-Octene, (%)
0.25	34.2	29.4	4.7	0.13	54.0
0.5	46.1	39.9	6.0	0.31	33.6
0.75	58.6	49.1	8.8	0.65	23.9
1.0	67.4	55.1	11.3	1.0	20.6
1.5	68.2	54.4	12.5	1.3	14.9
2.0	72.0	55.2	15.6	1.7	12.8
2.5	75.9	57.5	16.6	1.9	11.0
3.0	82.0	60.9	18.5	2.5	12.5
4.0	78.8	58.7	17.9	2.3	9.9
5.0	77.4	59.6	15.9	1.8	7.3
6.0	84.4	57.1	24.0	3.3	10.0

Maximum conversion reached by the reaction is 84.4 % in which only 57.1 % is dimer and 24 % trimer is found, which is a large amount. The reaction proceeds at a good rate, selectivity of the catalyst is observed not to be good. Figure 3.8 shows the trend of plot obtained with the kinetics data.

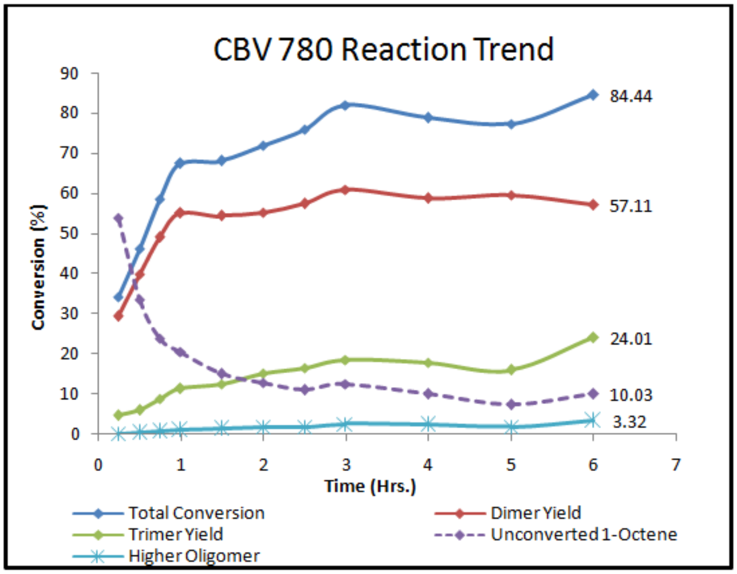


Figure 3.8: Plot showing % conversion vs. Time for dimerization reaction of 1-Octene with the catalyst-zeolyst CBV 780.

3.1.2 Catalyst Characterization procedure

Two well known characterization techniques for zeolites are applied to get insight into the nature of catalyst responsible for its behavior in experiments performed. The First one being Ammonia TPD (Temperature Programmed Desorption) technique, this technique is found to be very accurate to estimate the number and total acidic sites in zeolites. It works on the principle that the molecular size of ammonia allows it to penetrate in all the pores of the solid including micropores where it titrates the acidic sites of the catalyst owing to its basic nature. The information about number of acids sites, their strength and heterogeneity is recorded by the chemisorptions unit Micromeritics chemisorb 2750 used in R&D centre (RIL). Another method is to find out the BET surface area, this analysis technique works on the principle of BET theory which aims to explain the physical adsorption of gas molecules on a solid surfaces, this gives measurement of specific surface area of the solid. Micromeritrics ASAP 2020 unit is used in our laboratory for gas sorption analyses.

Another experiment done on all catalysts is to calculate the amount of weight gained by the catalysts after dimerization reaction. A weighing activity is done in which initial and final weights of the reaction content are recorded separately for the liquid and solid content in the reaction. The used catalyst is recovered very precisely by vacuum filtration, dried in vacuum oven for 24 hrs. and weighed, significant weight gain was observed in some catalysts. Table 3.9 shows the results of the characterization techniques applied to the catalysts.

Table 3.9: Characterization data and dimerization reaction results for various grades of zeolites.

Catalyst	Acidity (mmol/gm)	BET S.A. (m^2/gm)	Total Pore Vol. (cc/gm)	Avg. Pore Dia (Å)	Dimer Selectivity (%)	Dimer Yield (%)	% Wt. gain in dried catalyst
CBV 600	1.46	426	0.338	31.7	93.3	6.7	14.7
CBV 712 (NH_3 Cation)	1.51	670	0.490	29.3	93.3	9.0	14.6
CBV 712 (H-Cation)	1.67	627	0.471	30.1	92.6	29.4	29.5
CBV 720	1.33	676	0.499	29.5	84.5	54.5	45.8
CBV 780	0.56	724	0.536	29.6	70.4	57.1	65.0

It is evident from the results that CBV 600 and the two forms of CBV 712 show high selectivity for the dimer formation because of their lower pore volume but the combination of acidity and surface area of these catalysts is not the best match for our reaction. CBV 780 gives the highest conversion in our reaction this shows that CBV780 possesses the right combination of pore size and acidity to drive this reaction to high conversion, unfortunately it also promotes significant amount of trimer and higher formation. Also since a significant amount of weight gain is observed with CBV 780 it means loss of the reactant by trapping in the zeolite is high in this case. These factors make CBV 780 uneconomical for the process as separation of dimer from higher oligomers is a difficult cost intensive activity. Hence, from

Table 3.10: Characteristic data showing the comparison between fresh catalyst and used catalyst.

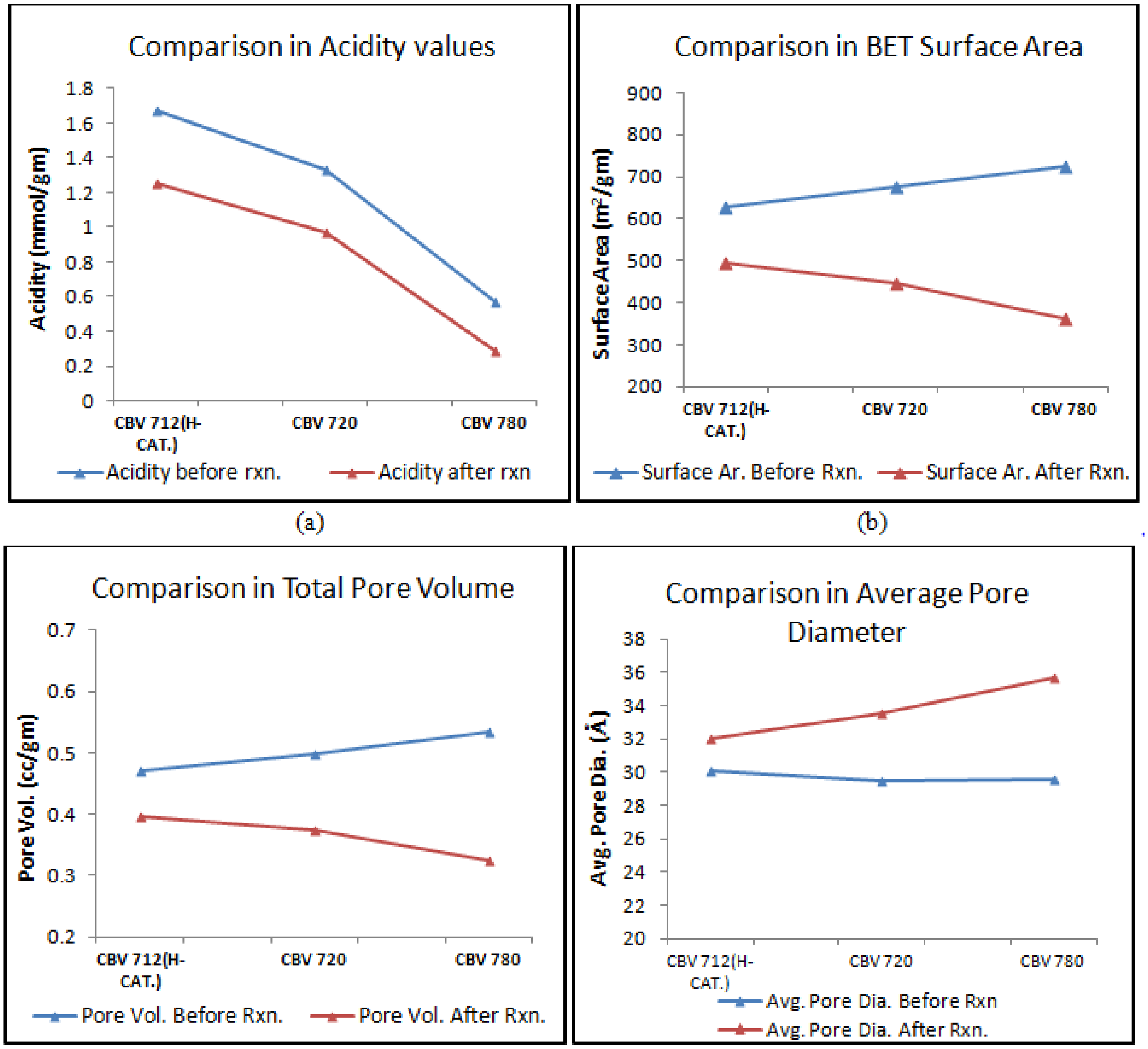
Catalyst	Acidity (mmol/gm)		BET surfacr area (m^2/gm)		Total Pore Vol. (cc/gm)		Avg. Pore Dia. (Å)	
	Before Rxn.	After Rxn.	Before Rxn.	After Rxn.	Before Rxn.	After Rxn.	Before Rxn.	After Rxn.
CBV 712 (H Cation)	1.67	1.25	626	494	0.471	0.396	30.0	32.0
CBV 720	1.34	0.97	676	447	0.499	0.375	29.5	33.5
CBV 780	0.57	0.29	724	363	0.536	0.325	29.6	35.7

these results it can be concluded that CBV 720 is the most suitable catalyst for dimerization reaction owing to its high dimer yield and good selectivity.

All the catalysts once used for reaction are recovered from the reaction mixture through filtration and dried for one day in vaccuum oven, now the above mentioned two characterization techniques are applied to these catalysts. Interesting trends have been observed in the properties of the fresh and used catalyst.

As expected after the reaction, acidity, surface area and pore volume of the catalysts reduce as these sites are occupied by the entrapped reactants/products/intermediates. Average pore dia. Of the catalyst increases after reaction because of unavailability of the micropores after one reaction cycle, now only meso-pores and macropores contribute to the average pore dia value. These trends can be better visualized in the form of graphs shown in Figure 3.9.

Next step in characterization is the regeneration of used catalyst; the catalyst is recovered from the reaction material after completion of one reaction cycle by the procedure mentioned earlier. The best way to regenerate a zeolite with high silicon to aluminium ratio is to oxidize the adsorbed organic material in a controlled fashion so that the silicon to aluminium ratio is not disturbed by local hot spots that can be generated by rapid burning. A stainless steel column 2 cm in dia. is filled with the degenerated catalyst, placed inside an insulated heating chamber and equipped with constant air supply. The temperature required for regenerating the used catalyst is set in the temperature programmer. Column attains a temp. of 80°C in first 20 minutes, in next 8 hours. column attains a temperature of 560 °C and remains at this temperature for 3 hrs. afterwards the program turns the heating device off. Hence, it takes approx. 12 hours to get regenerated zeolyte catalyst for further experimentation. Characterization and reaction data for the regenerated catalysts is mentioned in Table 3.11.



(a) (b)

(c) (d)

Figure 3.9: Plots showing the comparison between characteristics of the fresh catalysts and used catalyst (a) Acidity vs. Catalyst (b) BET vs. Catalyst (c) Pore Volume vs. Catalyst (d) Average Pore Diameter vs. Catalyst.

Table 3.12: Characterization data and dimerization reaction yield for regenerated catalysts.

Catalyst	Acidity (mmole/gm)			BET surface area (m^2/gm)			Dimer Yield %
	Fresh	Reg.	%	fresh	Reg.	%	(Reg./fresh)×100
CBV 712 (H cation)	1.67	1.42	84.8	627	555	88.5	70.4
CBV 720	1.33	1.07	80.2	676	684.7	100	100.0
CBV 780	0.57	0.32	55.8	724	607.8	83.9	87.6

It is evident from the data that approx. 80% acidity and 90% surface area is regenerated after one reaction cycle for CBV 712 (H cation) and CBV 720 catalysts. CBV 720 has surprisingly shown as much dimer yield as obtained with fresh catalyst thus, it can be concluded from all of the experimentation and characterization that CBV 720 is the best zeolite among various other grades for dimerization of olefins.

3.2 Dimerization Reaction with CBV 720: Selection of parameters and Kinetics of the reaction.

In this section detailed experimental results for dimerization of 1-Decene, 1-Octene, 2-Octene, Mixture of two isomers of Octene, 2-Heptene and Dodecene are illustrated and discussed. The reaction between Olefins to produce dimers (C_{14}, C_{16}, C_{20}, C_{24}) is an endothermic reaction optimum temperature for which is determined experimentally. The catalyst used is Zeolyst-CBV 720 since it was identified as the best catalyst in the earlier section; it is an acidic molecular sieve that selectively favors production of dimer of the subsequent olefin and minimizes formation of higher oligomers viz. trimer, tetramer. The catalyst is activated by heating it at 350 °C for 4 hours in a closed muffle furnace. This activated catalyst is sealed and stored as to prevent moisture from deactivating the catalyst.

3.2.1 Reaction operating parameters analysis

In the following section experimental results of dimerization of 1-Decene and 1-Octene in the presence of Zeolyst CBV 720 catalyst are used to find out the duration of reaction, optimum moisture content of reactants, best temperature for the reaction and optimum amount of catalyst to be used.

3.2.1.1 Dimerization reaction parameter study with 1-Decene

The Radely reactor is set to attain the required temperature for the reaction. As soon as the temperature is attained in the reactor; the reaction flask is fitted in the reactor and stirrer speed is set to 550 rpm. The reaction content consists of an accurately weighed amount of 1-Decene and the catalyst.

- Weight of 1-decene: 10 gm.
- Variation in moisture level of reactant:

    →1-Decene; as obtained from commercial source

    →Dry Decene (Dried in molecular sieves for 24 hr.)

    →Decene added with two drops of water (0.09 gm.)

- Variation in reaction temperatures: 105 °C, 120 °C, 135 °C

- Weight of Catalyst: 1 gm, 0.5 gm, 1.5 gm

$$\underset{(1-Decene)}{nC_{10}C_{20}} \xrightarrow{CBV720} C_{20}H_{40} + HigherOligomers + Un - reactedDecene \qquad (3.8)$$

Sample study to collect the experimental data and to observe the reaction kinetics is done at pre-decided time intervals. The transparent organic layer of the product floats above the reaction content; three to four drops of this layer is carefully taken with the help of a pipette in a sample vial, diluted and injected for GC analysis.

Objective 1: To Find the duration of the reaction.

First objective is to find out the duration till which reaction proceeds at an appreciable rate, for these three reactions are kept separately with reactants varying in moisture content at same temperature i.e. 120°C and with 1 gram of catalyst for every 10 gram of reactant.

Table 3.13: Conversion data for dimerization reaction with 1-Decene for 15 hours of reaction

	1-Decene	Dry Decene	Decene-Water
Time	% Conversion at 120°C and 1 gm. catalyst		
3hr.	26.6	15.2	20.9
6hr.	31.02	18.8	31.3
9hr.	35.8	18.3	32.15
15hr.	37.2	16.25	34.9

Observation: $<$90% conversion of reaction occurs till 6 hours. After 6 hours there is an insignificant increase in the conversion levels up-to 15 hours of the reaction.

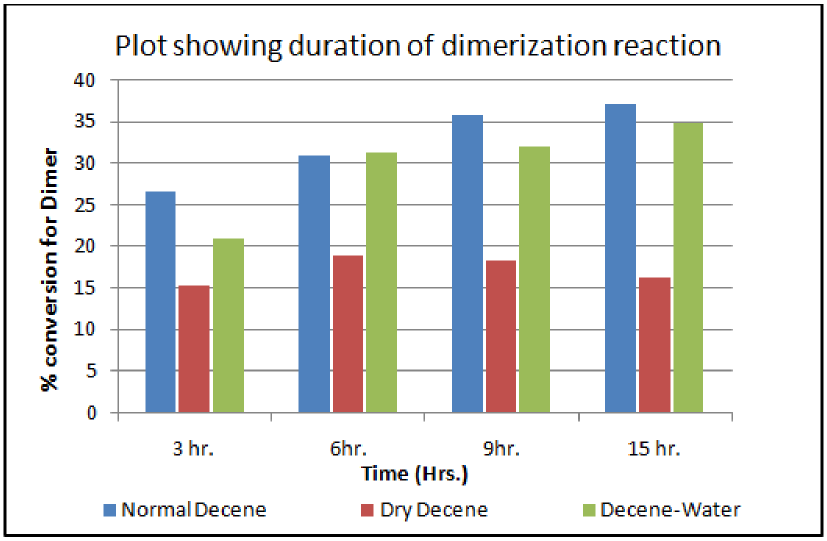


Figure 3.10: Plot showing extent of reaction in 15 hrs. for 1-Decene at different moisture levels.

Objective 2: To find the effect of moisture content of the reactant on the conversion data.

Second objective is to check the effect of moisture content of reactant (1-Decene) on the conversion of the reaction. For this three separate reactions are set up one with the decene as obtained from commercial source, second set contains decene dried with molecular sieves for 1 day; it has the lowest moisture content i.e. approx. 1 ppm and the third set contains decene added with 2 drops of distilled water (weight=0.98 gm.). Same temperature and amount of catalyst is used for all the reactions and are continued for 6 hours.

Table 3.14: Conversion data for dimerization of 1-Decene showing the effect of moisture content on the reaction

Percentage Conversion at 120°C and 1 gm. Catalyst						
Moisture content	Normal Decene		Dry Decene		Decene -Water	
Time	3 hr.	6 hr.	3 hr.	6 hr.	3 hr.	6 hr.
Set 1	26.6	31.02	15.2	18.8	20.9	31.3
Set 2	25.3	24.8	15.66	20.6	28.1	38.4
Set 3	25.9	22.6	30.5	32.12	12.1	13.7

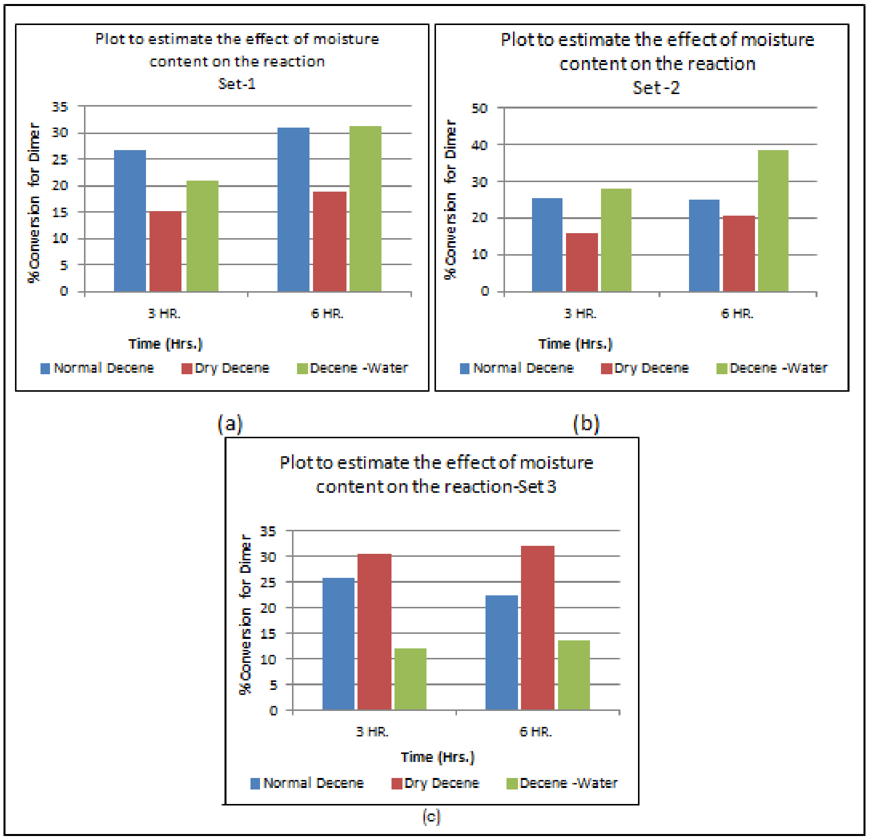


Figure 3.11: Plots showing the effect of moisture content on % conversion for 1-Decene dimerization reaction taken on three different days.

Observations: Decreasing or increasing the moisture content of 1-Decene has a considerable effect on the conversion of the reaction but no fixed trend is observed, atmospheric conditions also play a role in the initial moisture level of the reactant. A typical combination of atmospheric moisture level and reactant's moisture content seems to favor the reaction. A consistency in data has been observed if 1-Decene as obtained from commercial source is used, hence the kinetics of the reaction will be studied with the same.

Objective 3: To observe the effect of temperature on conversion in the reaction.

Temperature plays a key role in the endothermic dimerization reaction. To find out the most suitable temperature for the reaction again the reaction is kept in three separate round bottom flasks on radley reactor. Three sets of data are generated at three different temperatures mostly taken around the boiling point of the reactant.

Table 3.15: Conversion data for dimerization of 1-Decene at different temperatures.

Temperature variation data for 1-Decene Dimerization (1 gm. catalyst)			
6 hour data, °C	135	120	105
Normal Decene, %	37.9	31.02	25.3
Dry Decene, %	38.6	18.8	15.8
Decene Water, %	45.6	31.3	18.6

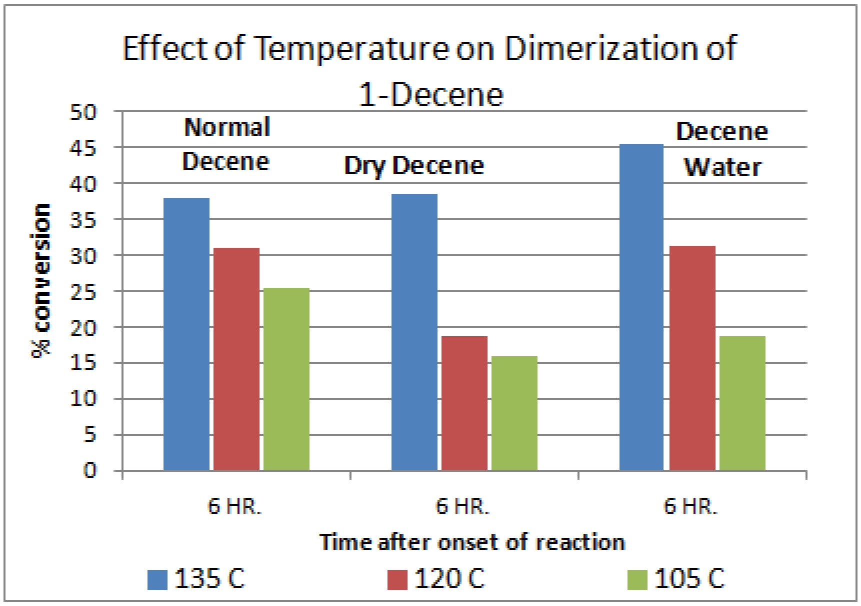


Figure 3.12: Plots showing the reaction conversion at different temperatures.

Observation: Highest conversion in the reaction is observed at 135 °C for normal 1-Decene.

Objective 4: To find out optimum amount of catalyst for good yield and to be used for further study at laboratory scale.

Use of optimum amount of catalyst is important for both good dimer yield and economics of the reaction. Three experiments are performed within a genuine range of amount of catalyst to be used per 10 gram of reactant keeping all other parameters constant.

Table 3.16: Dimerization reaction conversion data for varying amount of catalyst used with 1-Decene

Variation in amount of catalyst for reaction at 135°C				
Amount of Catalyst (grams)	Normal Decene		Dry Decene	
	3 hr.	6 hr.	3 hr.	6 hr.
0.5	10.1	17	9.3	9.8
1	37.1	40.6	42	35
1.5	64.8	77.9	47.6	60.4

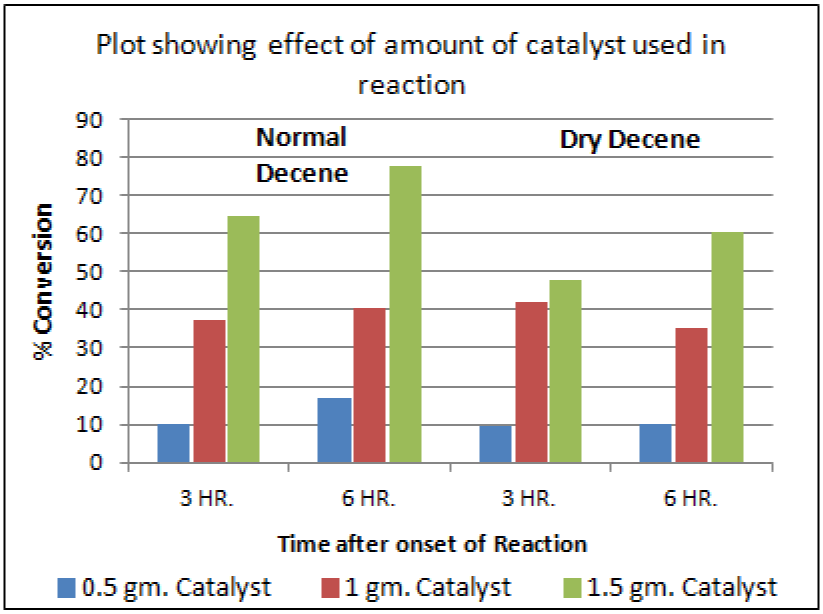


Figure 3.13: Plot showing the effect of amount of catalyst used on dimer yield.

Observation: Highest yield of dimer is obtained when 1.5 gram catalyst is used for all moisture levels of reactant.

3.2.1.2 Dimerization reaction parameter study with 1-Octene

Similar activity is performed with 1-Octene as reactant in the presence of catalyst CBV 720 to understand the effect of various parameters on the reaction and fix them to obtain a good yield of dimer and study the kinetics of the reaction. The general reaction setup is discussed as follows:-

- Weight of 1-Octene: 10 gm.
- Variation in moisture level of reactant:

  →1-Octene; as obtained from commercial source

  →Dry 1-Octene (Dried in molecular sieves for 24 hr.)

  →Variation in reaction temperatures: 95°C, 110°C, 125°C

- Variation in reaction temperatures: 105°C, 120°C, 135°C
- Weight of catalust: 1 gm, 0.5 gm, 1.5 gm

$$\underset{(1-Octene)}{nC_8H_{16}} \xrightarrow{CBV720} C_{16}H_{32} + Higher\,Oligomers + Un - reacted\,Octene \tag{3.9}$$

Objective1: To observe the effect of temperature and moisture content of reactant on conversion in the dimerization reaction.

Two reactions are kept separate containing 1-Octene at different moisture levels, one for 1-Octene as obtained from commercial source and has a moisture content approx. 137 ppm and the other set contains 1-Octene dried with molecular sieves for 1 day and has a moisture content approximately 1 ppm. Data has been generated at three temperatures selected around the boiling point of 1-Octene.

Table 3.17: : Reaction conversion data for dimerization of 1-Octene at different moisture content and temperatures.

% conversion for Octene with 1 gm catalyst				
Moisture Content	Normal 1-Octene		Dry 1-Octene	
Temp.(°C)	3 hr.	6 hr.	3 hr.	6 hr.
125	47.1	59.3	32.5	39.4
110	16	23	15	20
95	10.2	13.7	13.2	17.8

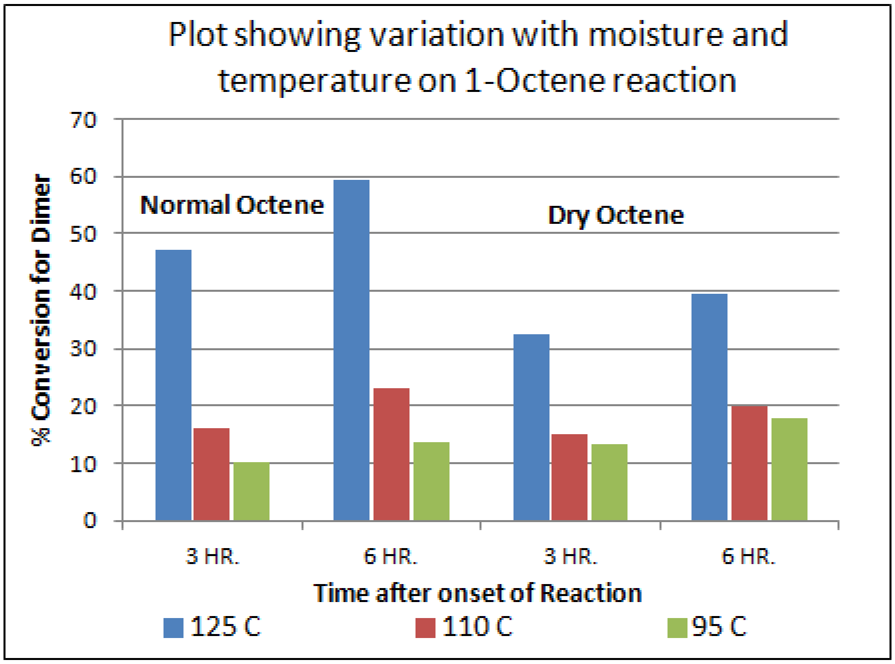


Figure 3.14: Plot showing the effect of moisture content of 1-Octene and temperature of reaction on the conversion.

Objective 2: To find out optimum amount of catalyst for good yield and to be used for further study at laboratory scale.

Table 3.18: : Dimerization reaction conversion data for varying amount of catalyst used with normal1-Octene.

% Conversion of 1-Octene at 125°C		
Catalyst (gm.)	3 hr.	6 hr.
1.5	55.31	67.46
1	47.1	59.3
0.5	15.1	27.8

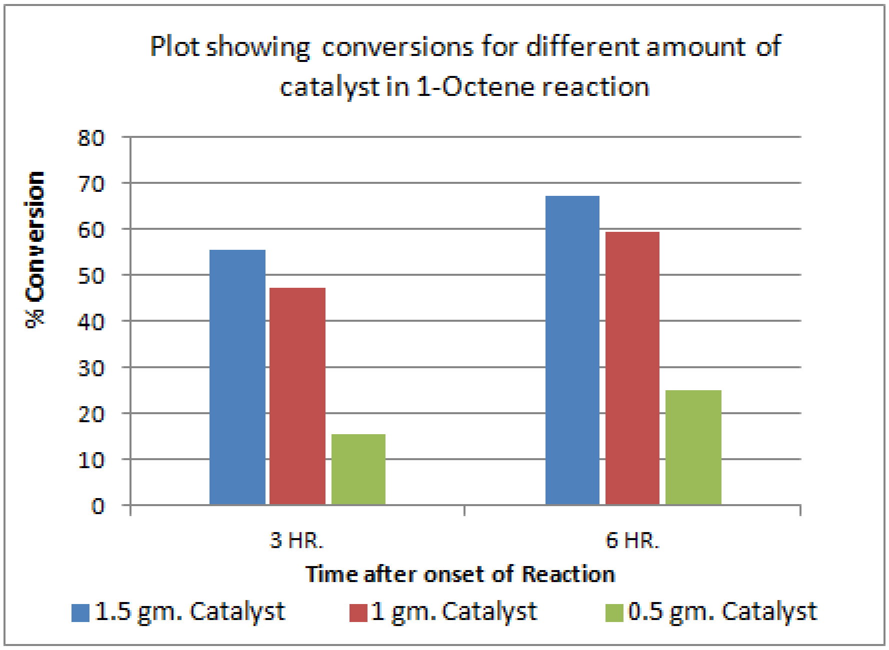


Figure 3.15: Plot showing the effect of amount of catalyst used on dimer yield.

Observation: Highest yield of dimer in dimerization of 1-Octene is obtained when 1.5 gram catalyst CBV 720 is used at 125°C.

Through the experimentation on varying the reaction parameters for 1-Decene and 1-Octene we have obtained best operating conditions for the dimerization reaction with respective olefins. Best Operating temperature for 1-Decene dimerization is found to be 135^{o}C along with 1.5 grams of catalyst for commercial grade decene. Commercial grade 1-Octene gives best dimer yield at 125^{o}C and 1.5 grams of catalyst. These operating conditions are widely applicable and will be used for reaction kinetics study in the following sections.

3.2.2 1-Decene Dimerization reaction Kinetics

For the kinetics study of the reaction, 10 gm. of commercial grade 1-Decene and 1.5 gram catalyst zeolite CBV 720 is taken in a radley RB and kept for 6 hours at 135°C and 550 rpm stirring speed. Reaction Sample analysis is done at predefined time intervals with maximum accuracy to obtain a well defined data for kinetics study of the reaction. Chromatogram of the reaction can be referred in the appendix.

Table 3.19: Reaction kinetics data for 1-Decene dimerization.

Time (Hrs.)	Total Conversion, %	Dimer Yield, %	Trimer Yield, %	Unconverted 1-Decene, %
0.25	26.0	24.8	1.2	31.3
0.5	32.1	30.5	1.6	32.0
0.75	36.7	35.1	1.7	33.0
1	40.2	38.5	1.7	26.0
1.5	40.6	38.4	2.2	22.0
2	47.4	44.7	2.7	23.2
2.5	49.5	48.4	1.0	21.6
3	47.2	43.7	3.4	22.9
4	50.1	47.6	2.5	17.8
6	54.9	51.8	3.1	13.7

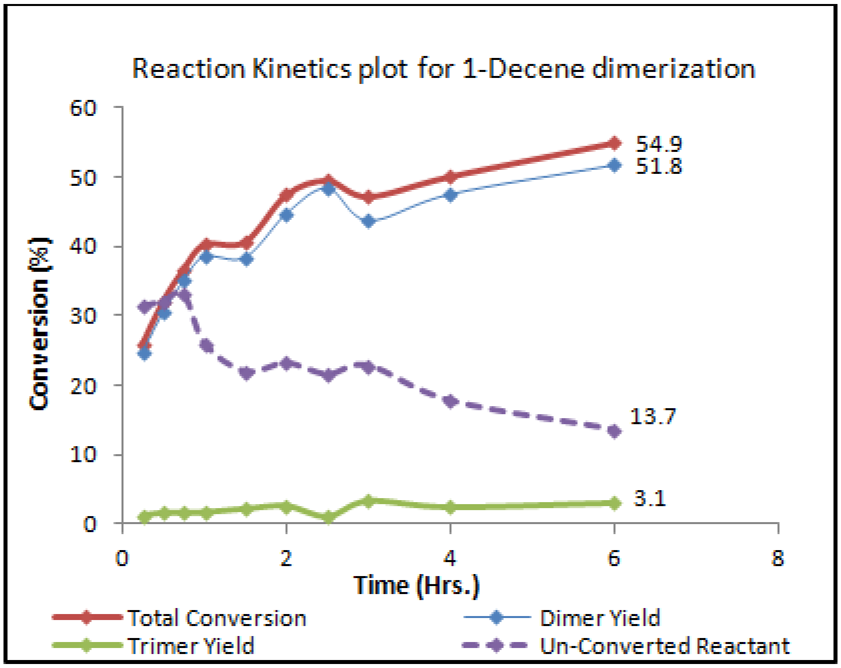


Figure 3.16: Reaction kinetics plot for dimerization of 1-Decene.

3.2.3 1-Octene Dimerization Reaction kinetics

For the kinetics study of the reaction, 10 gm. of commercial grade 1-Octene and 1.5 gram catalyst zeolite CBV 720 is taken in a radley RB and kept for 6 hours at 125°C and 550 rpm stirring speed. Reaction Sample analysis is done at predefined time intervals with maximum accuracy to obtain a well defined data for kinetics study of the reaction. Chromatogram of the reaction can be referred in the appendix.

Table 3.20: Reaction kinetics data for 1-Octene dimerization.

Time (Hrs.)	Total Conversion %	Dimer Yield %	Trimer Yield %	Unconverted 1-Octene %
0.25	20.5	18.7	1.8	76.0
0.5	26.6	24.3	2.3	59.1
0.75	33.5	30.9	3.3	58.9
1	45.1	40.2	4.9	52.5
1.5	48.3	42.7	5.6	51.3
2	53.9	47.6	6.4	44.0
3	55.3	48.6	6.8	37.3
4	61.0	53.4	7.6	39.7
6	67.5	57.9	9.5	30.6

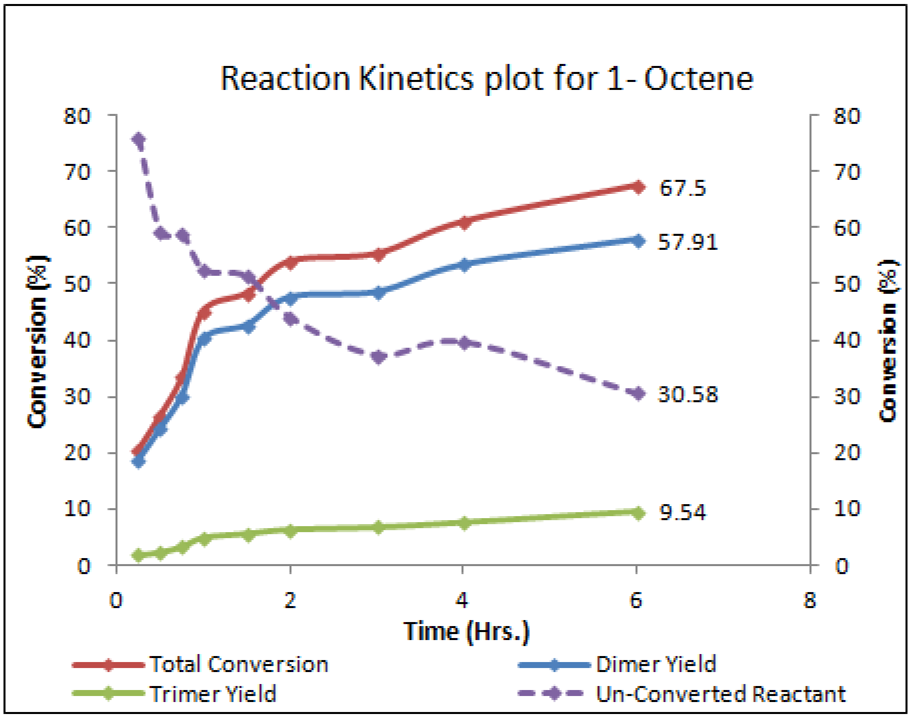


Figure 3.17: Reaction kinetics plot for dimerization of 1-Octene.

3.2.4 2-Octene Dimerization Reaction kinetics

For the kinetics study of the reaction, 10 gm. of commercial grade 2-Octene and 1.5 gram catalyst zeolite CBV 720 is taken in a radley RB and kept for 6 hours at 125°C and 550 rpm stirring speed. Reaction Sample analysis is done at predefined time intervals with maximum accuracy to obtain a well defined data for kinetics study of the reaction. Chromatogram of the reaction can be referred in the appendix.

Table 3.21: Reaction kinetics data for 2-Octene dimerization

Time (Hrs.)	Total Conversion,%	Dimer Yield,%	Trimer Yield,%	Unconverted 2-Octene,%
0.25	39.1	35.9	3.1	50.6
0.5	37.1	33.6	3.5	47.7
0.75	59.1	51.7	7.3	32.5
1	65.3	56.5	8.8	34.1
1.5	70.4	59.9	10.5	24.5
2	71.5	60.3	11.3	24.8
2.5	71.9	60.8	11.0	19.3
3	72.9	61.5	11.3	19.3
4	76.9	62.9	14.0	13.4
6	80.2	64.4	15.7	11.5

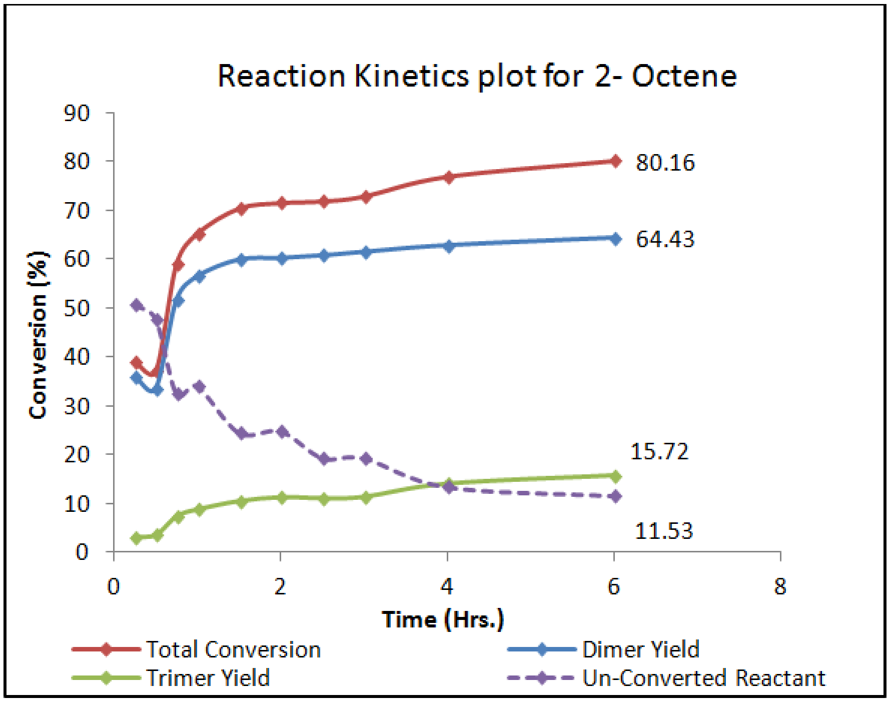


Figure 3.18: Reaction kinetics plot for dimerization of 2-Octene

3.2.5 1-Octene + 2-Octene Dimerization Reaction kinetics

For the kinetics study of the reaction 5 gm. 2-Octene and 5 gm. 1-Octene is taken with 1.5 gm. catalyst zeolyst CBV 720 in a radley RB and kept for 6 hrs. of reaction at 125°C with a magnetic bar for agitation at 550 rpm. Reaction sample analysis is done at predefined time intervals with maximum accuracy to obtain a well defined data for kinetics study of the reaction. Chromatogram of the reaction can be referred in the appendix.

Table 3.22: Reaction kinetics data for Octene isomer mixture dimerization.

Time (Hrs.)	Total Conversion,%	Dimer Yield,%	Trimer Yield,%	Unconverted Octene mix.,%
0.25	39.1	35.9	3.1	50.6
0.5	37.1	33.6	3.5	47.7
0.75	59.1	51.7	7.3	32.5
1	65.3	56.5	8.8	34.1
1.5	70.4	59.9	10.5	24.5
2	71.5	60.3	11.3	24.8
2.5	71.9	60.8	11.0	19.3
3	72.9	61.5	11.3	19.3
4	76.9	62.9	14.0	13.4
6	80.2	64.4	15.7	11.5

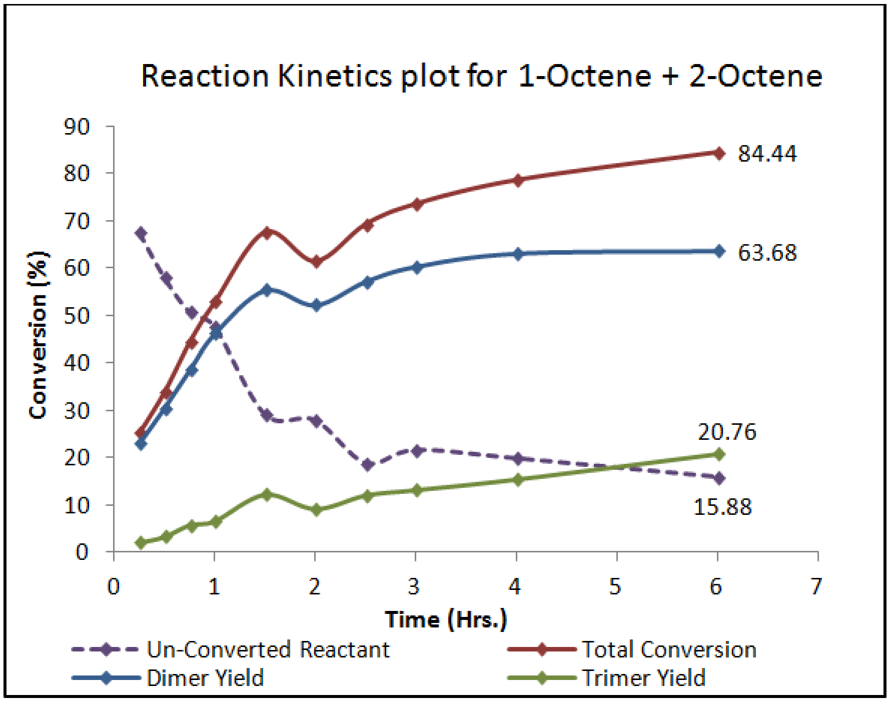


Figure 3.19: Reaction kinetics plot for dimerization of Octene isomer mixture.

3.2.6 2-Heptene Dimerization Reaction Kinetics

For the kinetics study of the reaction 10 gm. of 2-Heptene and 1.5 gram catalyst zeolite CBV 720 is taken in a radley RB and kept 6 hrs. for reaction at 95°C with a magnetic bar at 550 rpm. Reaction sample analysis is done at predefined time intervals with maximum accuracy to obtain a well defined data for kinetics study of the reaction. Chromatogram of the reaction can be referred in the the appendix.

Table 3.23: Reaction kinetics data for 2-Heptene dimerization

Time (Hrs.)	Total conversion,%
0.25	1.1
0.75	1.1
1	1.3
1.5	1.3
3	1.7
4	3.7
5	3.8
6	3.9

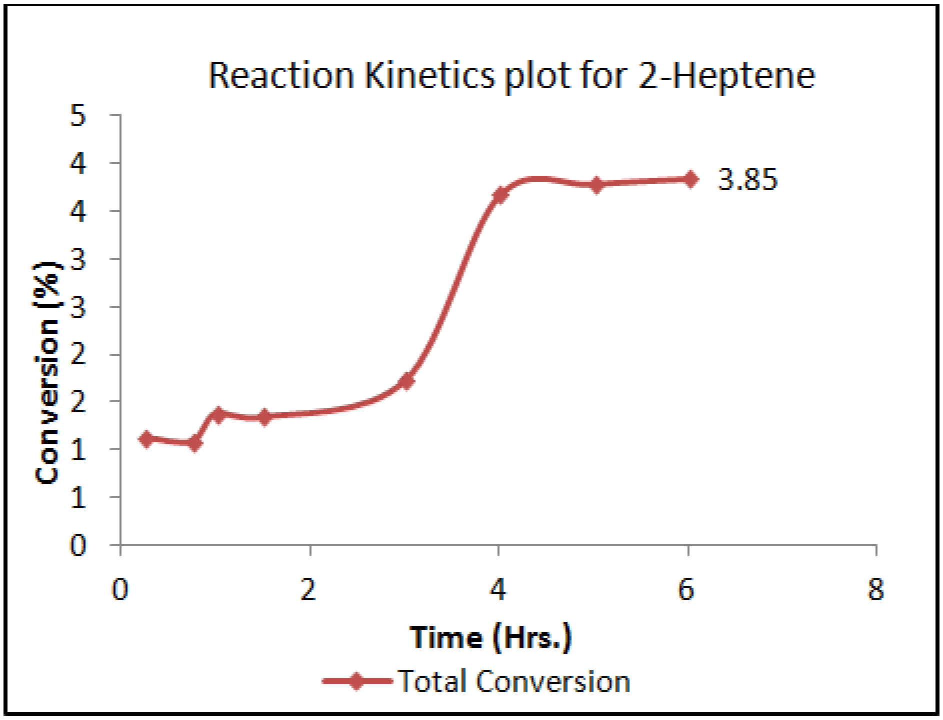


Figure 3.20: Reaction kinetics plot for dimerization of Octene isomer mixture.

3.2.7 Dodecene Dimerization Reaction Kinetics

For the kinetics study of the reaction 10 gm. dodecene and 1.5 gm. catalyst zeolite CBV 720 is taken in a radley RB and kept for 6 hours for reaction at 135°C with a magnetic bar at 550 rpm. Reaction sample analysis is done at predefined time intervals with maximum accuracy to obtain a well defined data for kinetics study of the reaction. It is observed that the product peak for dodecene reaction sits below the reactant peak, thus the product yield cannot be calculated with the help of peak integration in the chromatogram. Another method is applied to estimate the product yield i.e. the final reaction mixture is distilled to separate the product and the weight % of product is calculated as follows:

- Initial weight of reactant (Dodecene) = 30 gm
- Weight of product recovered after distillation = 4.466 gm.
- Thus, % conversion = 14.88 %

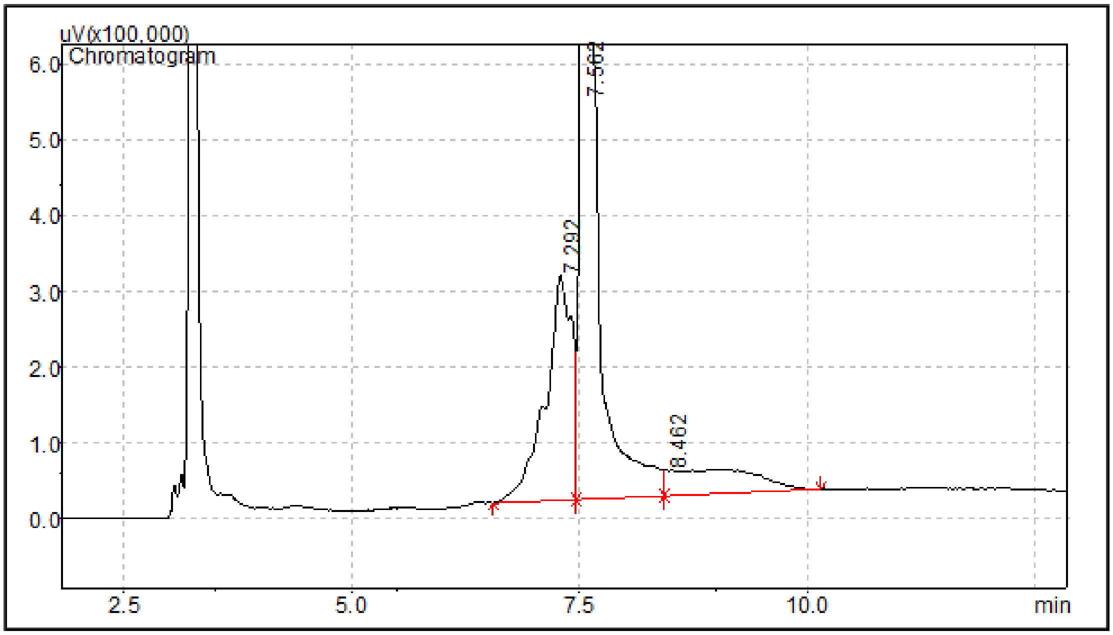


Figure 3.21: Chromatogram showing the retention time of pure Dodecene.

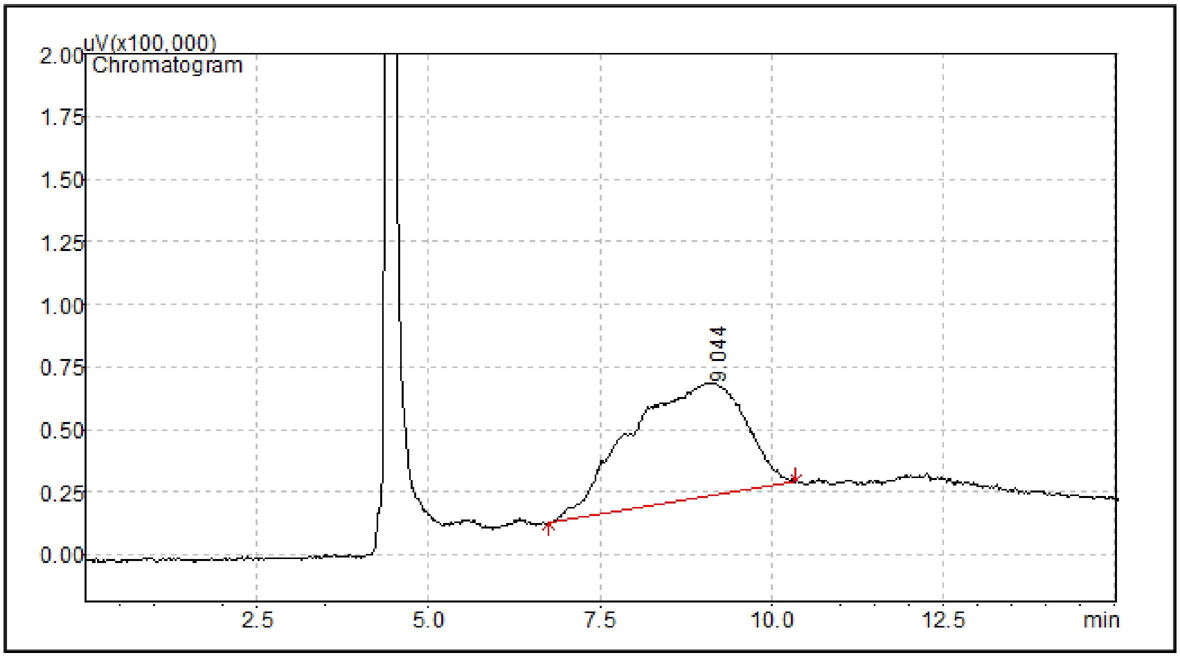


Figure 3.22: chromatogram showing the retention time of product after dimerization of dodecene.

3.3 ALKYLATION OF PHENOL

3.3.1 Experimental Setup for Alkylation of Phenol

The dimers prepared in the previous stage are distilled to get rid of the un-reacted reactant and trimer. The purified dimers are reacted with phenol as discussed in previous sections. The reaction sample study is done at predefined time intervals. Catalyst used for the reaction is macro-reticular cation exchange resin Amberlyst-36. It is found to be most useful catalyst among those studied for alkylation of phenol with an olefin. The ortho/para distribution in the alkylation of phenol with olefins is found to be a function of catalyst, reaction temperature and nature of olefin.

In the laboratory preparation of alkyl phenol accurately weight amounts of reactants and catalyst are taken in a Radley's round bottom flask. and kept for reaction at set temperature. Duration of the reaction is determined by observing the kinetic data of the reaction.

- Weight of Phenol used for reaction: 6.5 gm.
- Weight of Dimer used for reaction: 5 gm.
- Weight of catalyst used: 1gm.
- Temperature of the reaction: 125 °C
- Speed of stirrer: 650 r.p.m.

3.3.2 Reaction kinetics data for alkylation of phenol (AOP) with 1-Decene dimer

Firstly the standards of 1-Decene dimer are prepared with a range of weight ratios and GC analysis is performed for them. The results are put through the calculation as mentioned below and are plotted. This results in a linear plot which generates an equation of the straight line, the response factor for 1-Decene dimer is found from this equation. The response factor is used to calculate un-reacted reactant for the reactions involving 1-Decene dimer as a reactant.

Table 3.24: Standard sample data for 1-Decene dimer.

Decene Dimer Wt. (gm.)	Toluene Wt. (gm.)	Wt. Ratio (R1)	Peak Area Ratio (R2)	Z=R1/R2
0.033	0.158	0.21	0.15	1.43
0.041	0.158	0.26	0.10	2.64
0.071	0.154	0.46	0.21	2.24
0.081	0.156	0.52	0.24	2.22
0.115	0.158	0.73	0.39	1.87

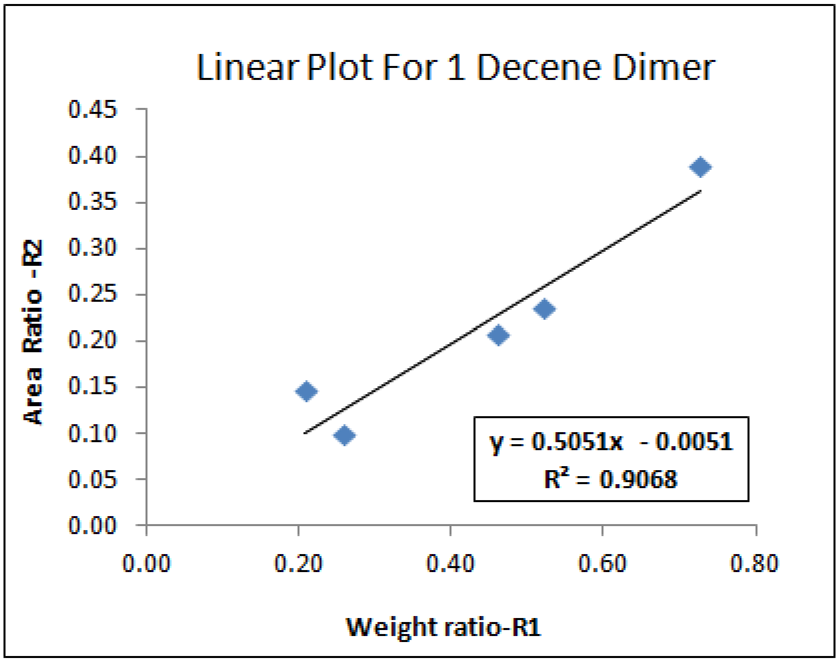


Figure 3.23: Linear Plot for 1-Decene dimer giving value of m=0.505.

The phenol ring is alkylated by 1-Decene dimer with a cationic mechanism offered by the highly acidic catalyst Amberlyst 36 used in the work. The highly branched long chain dimer attacks at the cationic site of the phenol and undergoes temporary movement in substitution site viz. ortho/para/meta sites to give the final alkylphenol. For our work, the catalyst is para position selective as this is the desired substitution site as discussed in literature review.

Table 3.25: Reaction kinetics data for alkylation of phenol with 1-Decene dimer

Time (Hrs.)	Conversion, %	Unconverted reactant, %
0.25	5.0	50.2
0.5	7.1	36.5
0.75	12.7	38.4
1	13.2	33.7
1.5	18.9	31.2
2	24.1	29.2
2.5	27.8	32.3
3	33.6	27.9
4	36.7	23.2
5	46.9	18.0
6	56.3	20.4
8	69.7	15.0

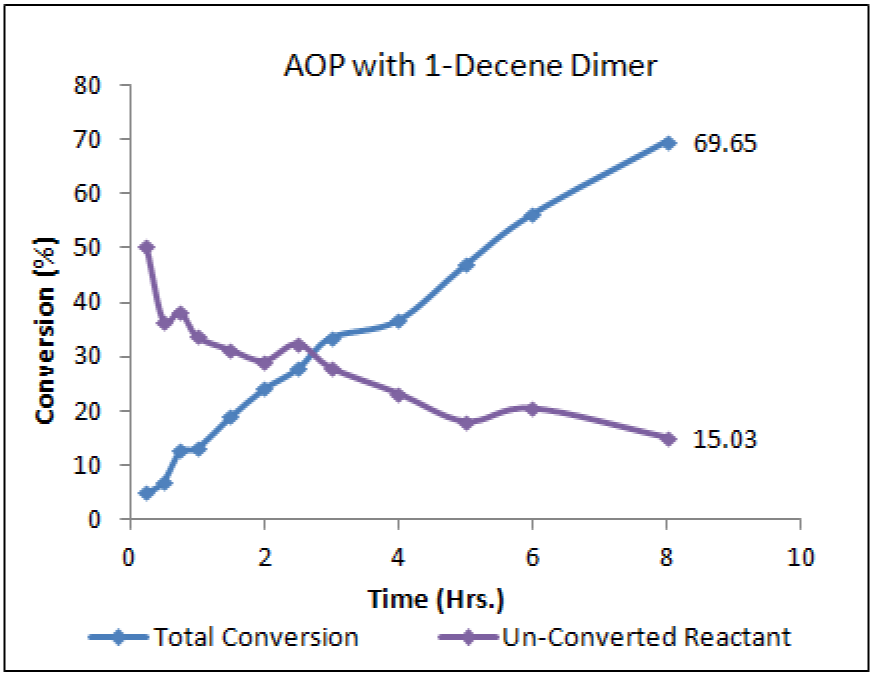


Figure 3.24: Reaction kinetics plot for alkylation of phenol with 1-Decene dimer

3.3.3 Reaction kinetics data for alkylation of phenol with 1-Octene dimer

The standards of pure 1-Octene dimer are prepared with a range of weight ratios and GC analysis is performed for them. The results are put through the calculation as mentioned below and are plotted. This results in a linear plot which generates an equation of the straight line, the response factor for 1-Octene dimer is found from this equation. The response factor is used to calculate unreacted reactant for the reactions involving 1-Octene dimer as a reactant. Table 3.24: Standard sample data for 1-Octene dimer.

Table 3.26: Standard sample data for 1-Octene dimer.

1-Octene Dimer Wt. (gm.)	Toluene Wt. (gm.)	Wt. Ratio (R1)	Peak Area Ratio (R2)	Z=R1/R2
0.032	0.167	0.19	0.13	1.47
0.063	0.191	0.33	0.24	1.36
0.071	0.208	0.34	0.23	1.50
0.104	0.228	0.46	0.31	1.46
0.160	0.317	0.51	0.35	1.45

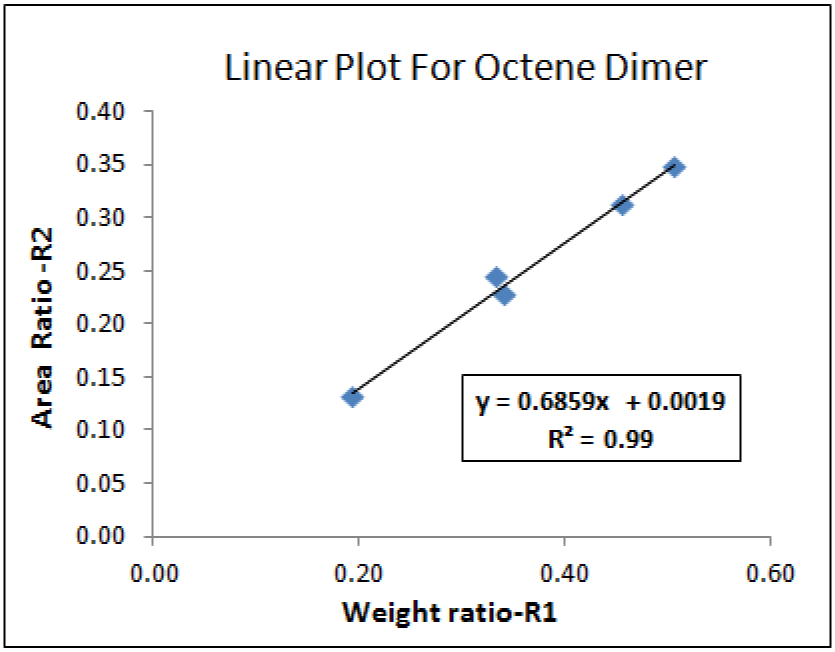


Figure 3.25: Linear Plot for 1-Octene dimer giving value of m=0.685.

1-Octene dimer also follows the same cationic mechanism as discussed above for 1-Decene dimer. Although the dimer of 1-Octene has a shorter chain with respect to that of 1-Decene dimer , thus a different value of conversion can be expected.

Table 3.27: Reaction kinetics data for alkylation of phenol with 1-Octene dimer.

Time (Hrs.)	Conversion, %	Unconverted reactant, %
0.5	9.9	67.0
0.75	17.8	63.9
1.0	21.6	64.4
1.5	25.0	53.3
2.0	38.1	49.5
2.5	40.8	50.6
3.0	53.5	48.5
4.0	64.3	34.4
6.0	72.2	30.2

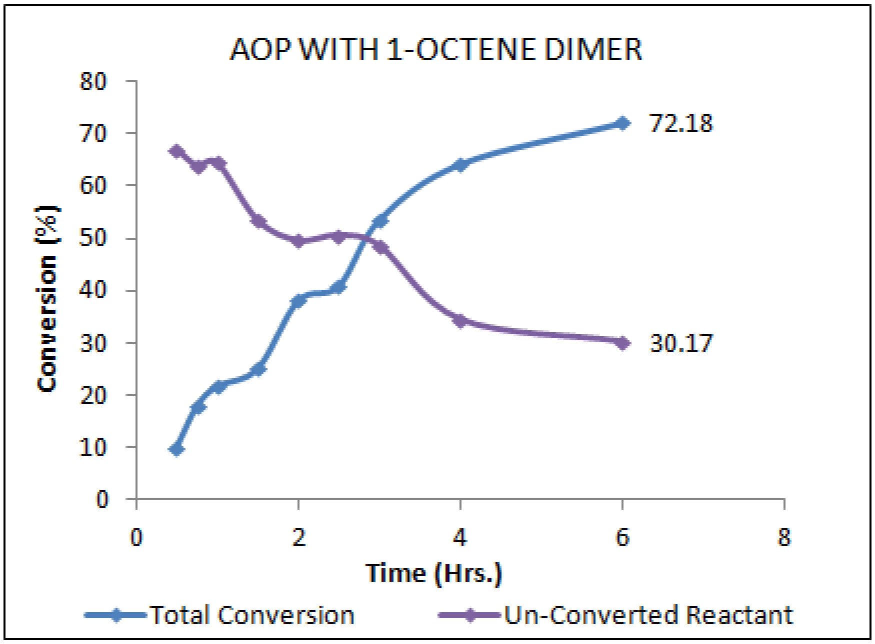


Figure 3.26: Reaction kinetics plot for alkylation of phenol with 1-Octene dimer.

3.3.4 Reaction kinetics data for alkylation of phenol with 2-Octene dimer

The response factor calculated for 1-Octene dimer is applicable for 2-Octene dimer also. 2-Octene dimer also follows the same cationic mechanism as discussed above for reaction with other dimers. The 2-Octene dimer being more internalized has a different structure as compared to 1-Octene dimer, also this creates a difference in chain length with respect to that of 1-Octene dimer , thus a different value of conversion can be expected.

Table 3.28: Reaction kinetics data for alkylation of phenol with 2-Octene dimer.

Time (Hrs.)	Conversion, %	Unconverted reactant, %
0.5	5.8	61.6
0.75	10.6	64.7
1	15.5	57.7
1.5	22.5	50.0
2	29.7	45.6
2.5	37.5	35.9
3	46.4	31.8
4	53.1	29.7
6	62.2	24.0

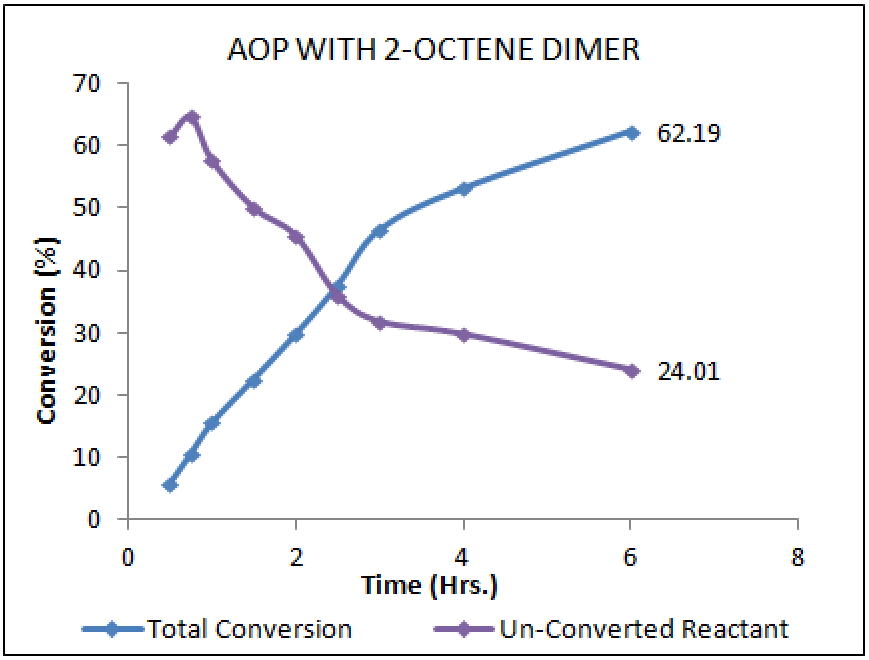


Figure 3.27: action kinetics plot for alkylation of phenol with 2-Octene dimer.

Using the same calculations as mentioned above the conversion of the reactants is calculated and also the unreacted with respect to dimer is calculated. Conversion equivalent to 1-Decene dimer i.e. 62.2% is obtained with an unconverted value of approximately 24% 2-Octene dimer.

Chapter 4

Results and discussions

An extensive study on zeolites has led us to some good understanding of this subject. Among the five zeolites studied, CBV 600 and CBV 712-ammonium cation form do not possess the right combination of characteristics required for dimerization of olefins in the given set of experimental conditions. CBV 712-hydrogen cation form is found to show high selectivity for dimer formation compared to the other zeolites studied, unfortunately the dimer yiled is in the higher 20 percentage. CBV 780 and CBV 720 have shown the best conversion results for the dimerization of olefins under given experimental conditions. Although CBV 780 shows the highest conversion values but it has a tendency to form more trimer and other higher oligomers which it ends up trapping. This behavior of CBV 780 is evident from the data of weight gain in catalyst after reaction. Weight gain is generally due to formation of higher oligomers of olefins which are subsequently trapped in the pores of zeolite. A significant loss of starting material and requirement of separation of higher oligomers from their respective dimers after the reaction makes this catalyst not a very good choice. The catalyst CBV 720 has shown appreciable dimer yield, good selectivity for dimer and highest regenerability values. Thus, CBV 720 is found to be the best combination of all the characteristics required in a catalyst for dimerization of olefins under the given set of experimental conditions.

The outcome of the experimental has led us to some interesting results about the kinetics of the reactions performed. The kinetics data sets obtained during the study has been used to fit to various rate equations which reveal some crucial things like the value of rate constant, analogy between conversion levels and rate of the reaction, effect of structures of reactant/ product/ intermediates on the reaction rate and effect of temperature on the rate of reaction.

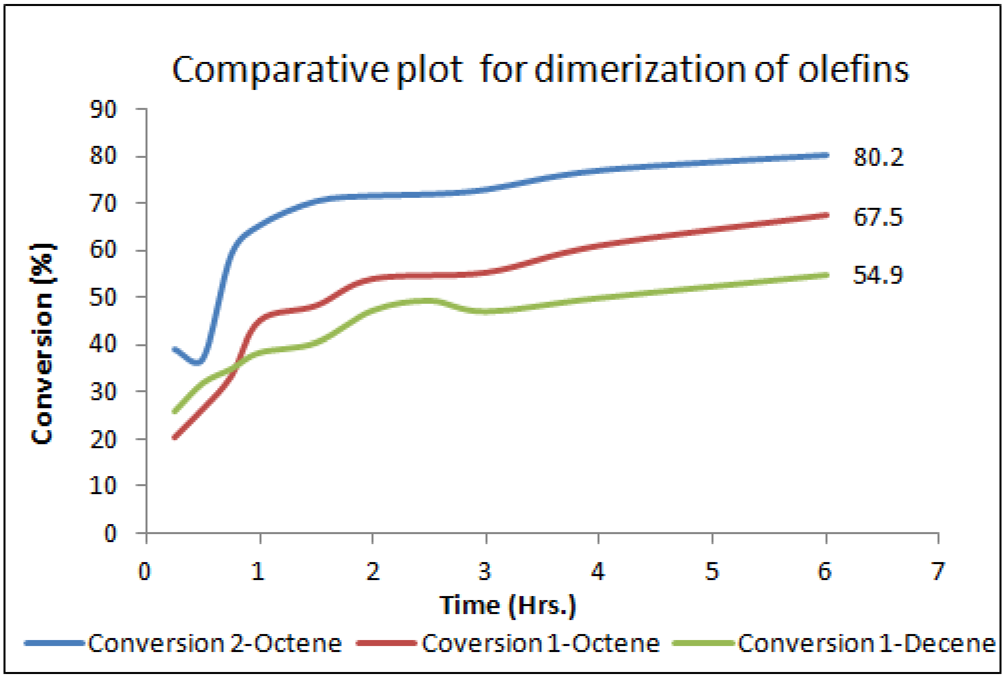


Figure 4.1: A comparative plot showing the dimerization results for all olefins.

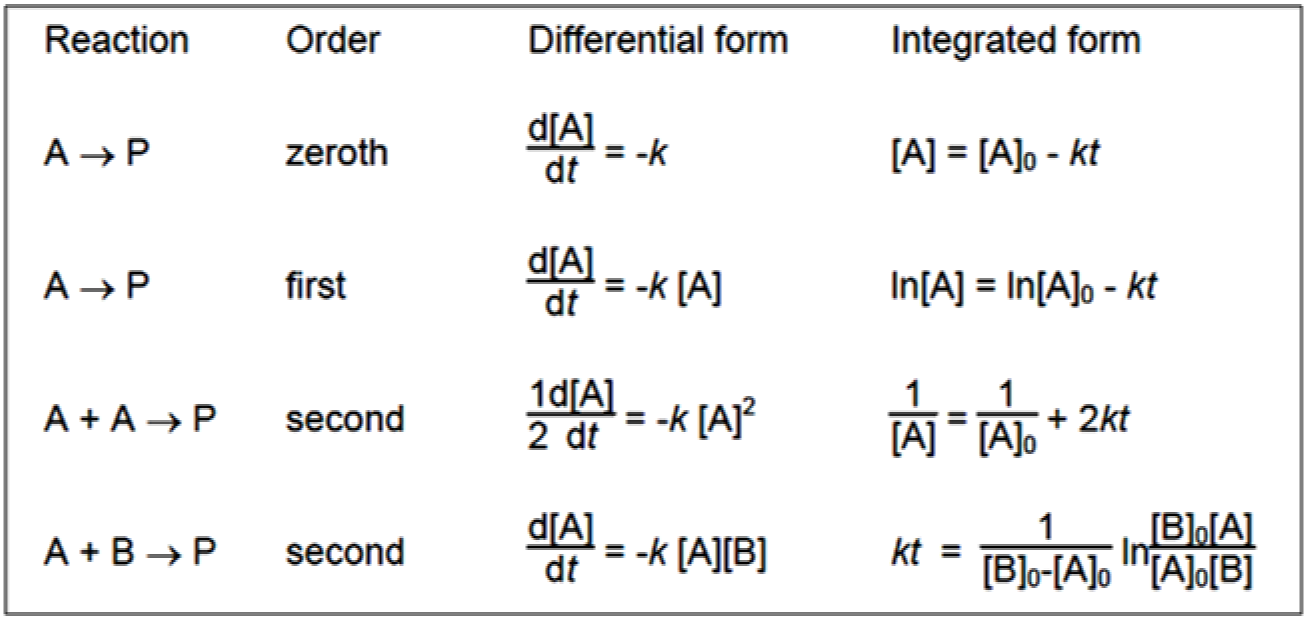
It has been found thatis known that dimerization of olefins done in the presence of zeolite catalysts is largely affected by the behavior of the olefin and product inside the catalyst pores [44], thus, making the pore size/ structure/distribution a deciding parameter in prediction of dimer yield and the extent of the reaction. To understand this in our case the kinetic data obtained was fit to different rate equations.

In order to study kinetics of the reactions some basic chemical laws are to be followed. The rate law is an expression relating the rate of a reaction to the concentrations of the chemical species present, which may include reactants, products, and catalysts. Many reactions follow a simple rate law, which takes the form :

$$\nu = K[A]^a[B]^b[c]^c \tag{4.1}$$

The rate is proportional to the concentrations of the reactants each raised to some power. The constant of proportionality, k, is called the rate constant.

A rate law is a differential equation that describes the rate of change of a reactant (or product) concentration with time. If we integrate the rate law then we obtain an expression for the concentration as a function of time, which is generally the type of data obtained in an experiment [45]



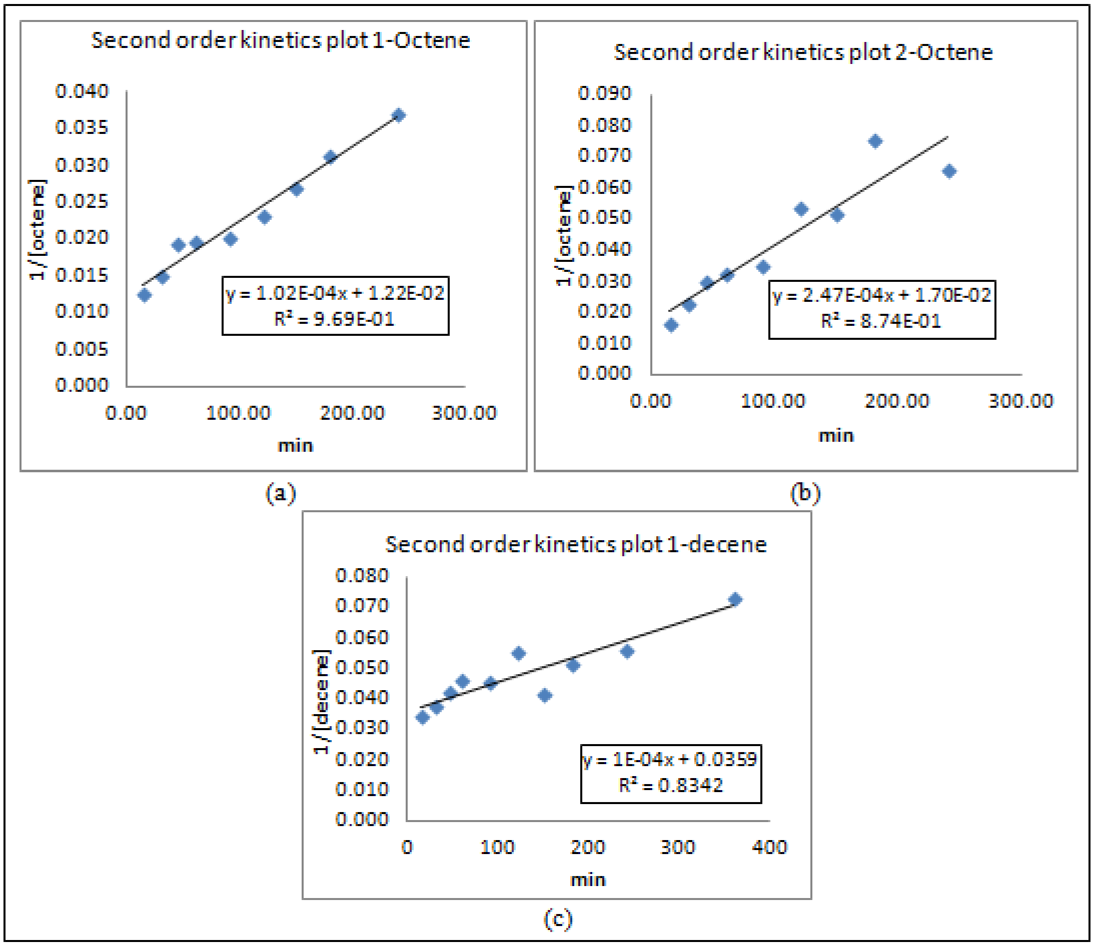
Reaction	Order	Differential form	Integrated form
$A \rightarrow P$	zeroth	$\frac{d[A]}{dt} = -k$	$[A] = [A]_0 - kt$
$A \rightarrow P$	first	$\frac{d[A]}{dt} = -k\,[A]$	$\ln[A] = \ln[A]_0 - kt$
$A + A \rightarrow P$	second	$\frac{1}{2}\frac{d[A]}{dt} = -k\,[A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + 2kt$
$A + B \rightarrow P$	second	$\frac{d[A]}{dt} = -k\,[A][B]$	$kt = \frac{1}{[B]_0-[A]_0} \ln\frac{[B]_0[A]}{[A]_0[B]}$

Figure 4.2: General Chemical reaction kinetic equations.

the case of dimerization reaction the overall equation looks like:

$$\underset{(Olefin)}{2C_nH_{2n}} \xrightarrow{CBV\,720} \underset{(Dimer)}{C_{2n}H_{4n}} + Higher\,Oligomers \tag{4.2}$$

It is clear from this equation that the dimerization reaction should be second order with respect to the olefin concentration. Thus the kinetic data obtained for 1-Octene , 2-Octene and 1-Decene were fit to a second order kinetic curve wherein a plot of the drop in initial olefin concentration represented by 1/[olefin] was plotted against tim



(a) (b)

(c)

Figure 4.3: Dimerization reaction data fitting to rate equation.

Table 4.1: Table showing the rate constant values for dimerization reactions.

Reaction	Rate constant obtained, ($mol^{-1}min^{-1}$)	Order of the reaction
Dimerization of 1-Octene	1×10^{-4}	2nd Order
Dimerization of 1-Decene	1×10^{-4}	2nd Order
Dimerization of 2-Octene	2×10^{-4}	2nd Order

As evident from the conversion data for 1-Octene and 1-Decene dimerization reaction, 1-Octene has shown better results although its reaction operating temperature is 125°C which is 10°C lower than that for 1-Decene dimerization reaction i.e. 135°C. For every 10°C rise in temperature, the rate of reaction must double according to laws of chemical reaction kinetics. Thus the actual rate constant for 1-Octene dimerization is in effect double that observed for 1-Decene, if the reactions are carried out at same temperatures. On comparing 1-Octene versus 2-Octene it has been observed that the rate of dimerization of 2-Octene is double

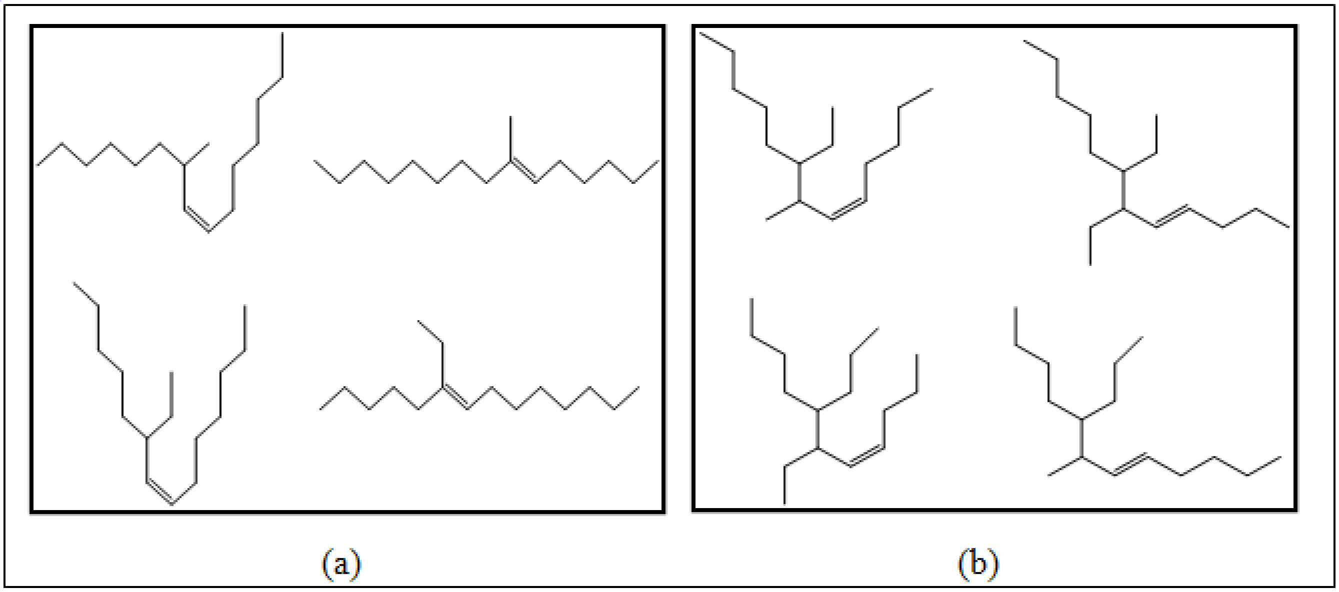


Figure 4.4: Tentative dimeric structures for 1-Octene (a) and 2-Octene (b)

that of 1-Octene dimerization. We have also studied other long chain olefins like 1-dodecene which shows very low conversion of around 15% at 135°C in 6h.

Our interpretation to this behavior lies in the activity of olefin chains inside the zeolite catalyst. The rate controlling steps of dimerization reaction can be the entry of the olefin into the pores and rate of exit of product from the pores. 2-Octene forms dimers with lesser space volume i.e. more internalized structures are formed as compared to 1-Octene dimers which may have larger space volume. This behavior can be illustrated by some tentative structures of respective dimers as shown in fig.4.4. This phenomenon makes it easy for 2-Octene dimer to exit from the pores of zeolite and make the active sites available for more chains to come and react. This fact contributes to faster rate of formation of dimers for internal olefins as compare to terminal olefins.

Also as the carbon number of terminal olefin increases as in the case of 1-Decene and 1-Dodecene as compared to 1-Octene, the entry of olefin into the active sites itself becomes a slow step thereby indicating slower kinetics for 1-Decene over 1-Octene and low conversion in the case of 1-dodecene.

A comparative plot for alkylation of phenol with all dimers leads us to an observation of the possible reaction mechanism.

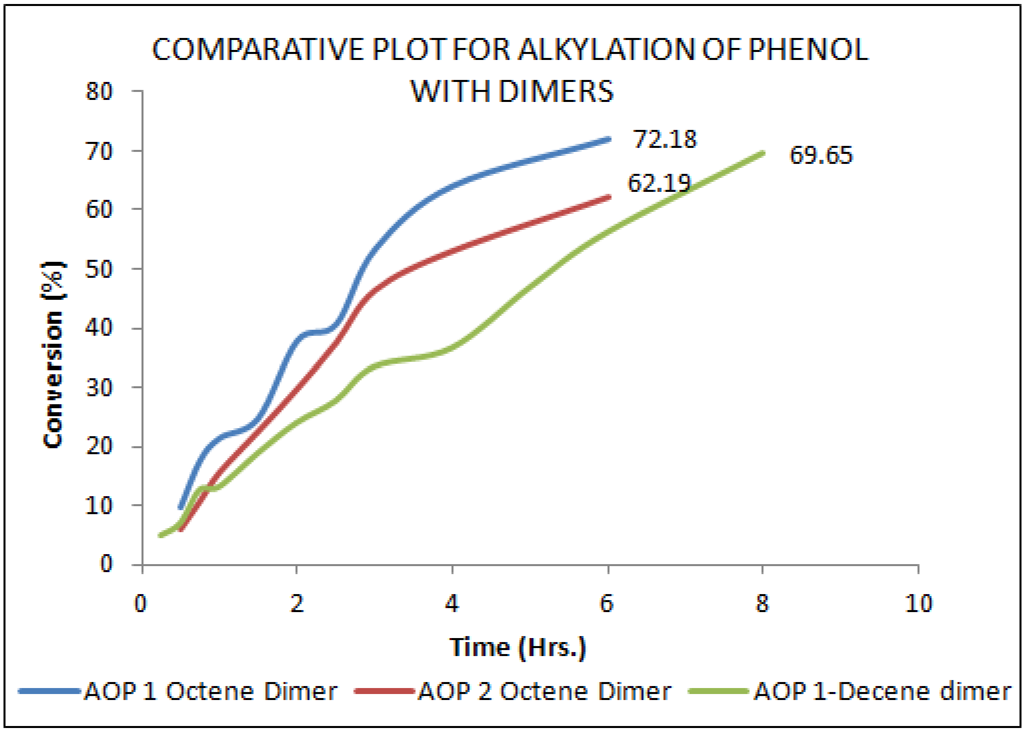


Figure 4.5: Plot showing comparison in conversion values for alkylation of phenol with various dimers.

The alkylation of phenol is done in the presence of Amberlyst-36 dry which is a strong acidic catalyst. The overall reaction for alkylation of phenol is as given below:

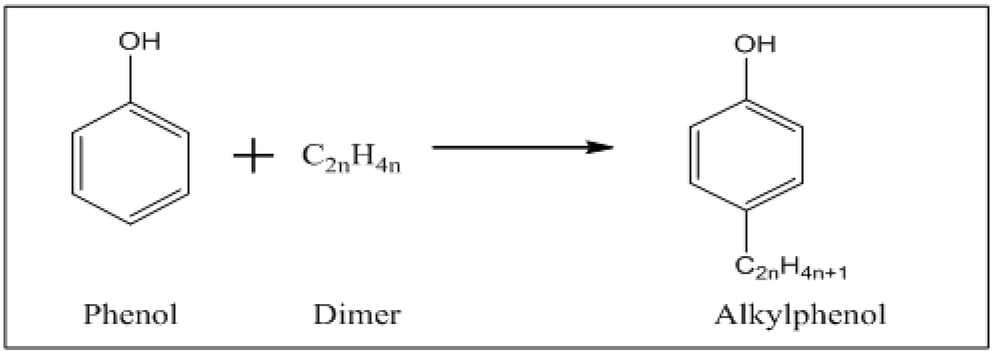


Figure 4.6: Reaction scheme showing alkylation of phenol with dimer

It is clear from this equation that the reaction should be second order and concentration of both the reactants must determine the rate of the reaction. In our reaction excess phenol has been taken i.e. 3 parts phenol for 1 part of dimer in order to avoid the side reaction forming higher alkylates of the phenol. Thus it is expected that the reaction will convert into a pseudo first order reaction. The kinetic data obtained fordrop in olefin concentration with 1-Octene dimer, 2-Octene dimer and 1-Decene dimer were fit tofirst order kinetic curve wherein a plot of the drop in initial olefin concentration represented by ln[olefin] was plotted against time.

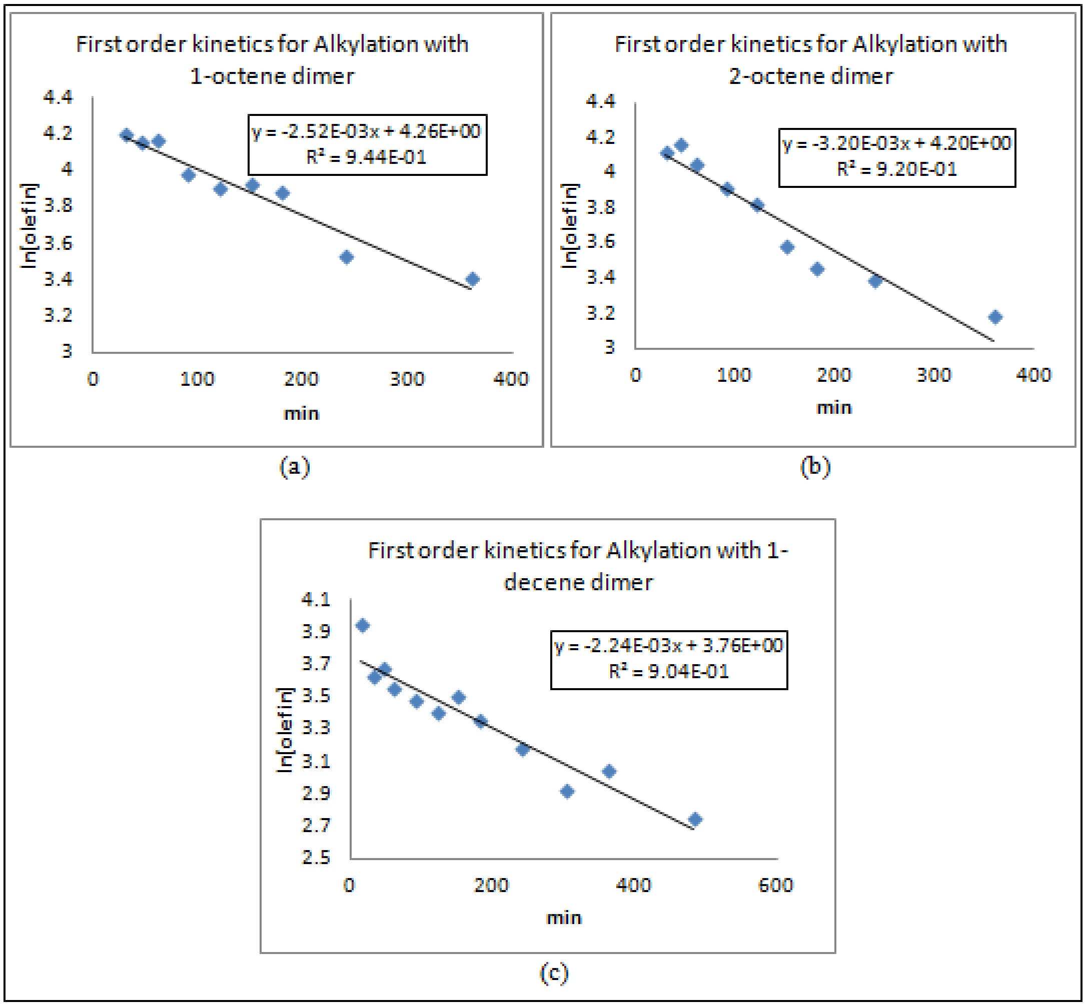


Figure 4.7: Alkylation reaction data fitting to rate equation.

Table 4.2: Table showing the rate constant values for AOP reaction

Reaction	Rate constant obtained, (min^{-1})	Order of the reaction
AOP with 1-Octene dimer	2.2×10^{-3}	1st Order
AOP with 1-Decene dimer	2.5×10^{-3}	1st Order
AOP with 2-Octene dimer	3.2×10^{-3}	1st Order

As evident from the conversion data, 1-Octene dimer has shown the highest conversion results closely followed by 1-Decene dimer in alkylation of phenol. 2-Octene on the other hand shows lower conversion values in the same experimental conditions as compared to dimers of alpha olefins. The rate constants obtained for the drop in olefin concentration in all three cases are similar within experimental error. This is quite surprising as the alkylation was expected to be difficult with the 2-Octene dimer as compared to the 1-Octene dimer or 1-Decene dimer. This is because in the case of the 2-Octene dimer the olefin should be more sterically hindered as compared to the α-olefin dimer cases. The overall conversion with 2-Octene dimer is lower than that seen with 1-octene dimer, to understand this better a structural characterization of the individual dimers were carried out using quantitative ^{13}C NMR [46][47].

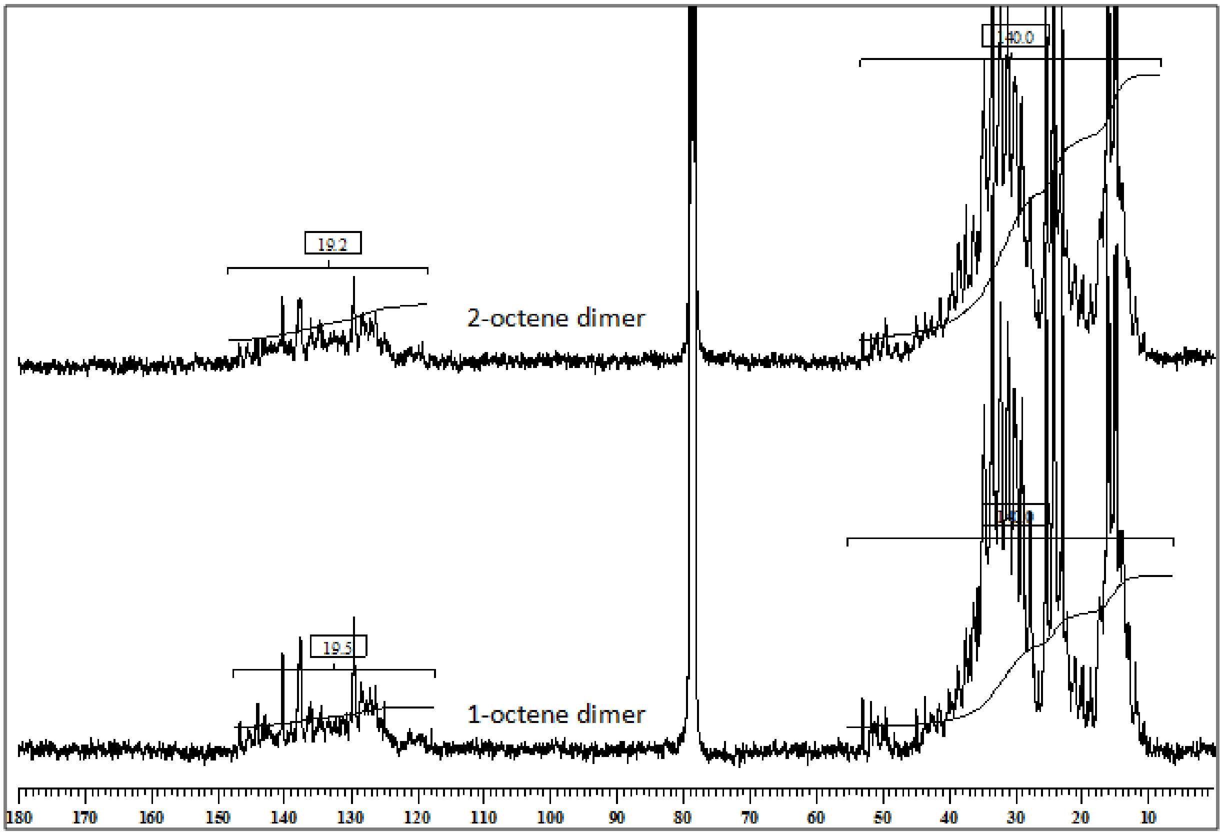


Figure 4.8: NMR results of 1-Octene and 2-Octene dimres.

It can be clearly seen from the quantitative ^{13}C NMR data of 1-Octene dimer and 2-Octene dimer that the olefins present in 1-Octene dimer is higher than that present in 2-Octene dimer. Although we do not have an explanation for this, we have found that this is further supported by the fact that the bromine number for 1-Octene dimer is around 68 gBr/100g and that of 2-Octene dimer is around 64 gBr/100g which is expected from the intergrals, when the theoretical bromine number of the octene dimer is 71 g Br/100g of sample. We expect that the lower total conversion with the 2-Octene dimer towards alkylation is due to this lower olefin content of approximately 5 – 7 %. Further a detailed comparison of the 13C NMR data between 1-Octene dimer and 2-Octene dimer reveals that the total quaternary olefin present in both the dimers is around 31% each. We also can see that the 2-Octene dimer is more branched and has around 7% CH units, 67% CH_2 units and 26% CH_3 units whereas the 1-Octene dimer has 4% CH units, 67% CH_2 units and 29% CH_3 units in the region between 55 – 10 ppm.

To understand the final alkylphenol formed with the 1-Octene dimer, 2-Octene dimer and 1-Decene dimer better their ^{13}C NMR was recorded and the spectra were integrated even though it had not been recorded in the quantitative ^{13}C NMR mode. The most important information that we can get from this is that the ratio of ortho to para isomers of the alkylphenol is about 11% for 1-Octene dimer, 10% for 2-Octene dimer and about 9% for 1-Decene dimer. This probably implies when the olefin is more sterically hindered the para isomer is the preferred isomer to be formed.

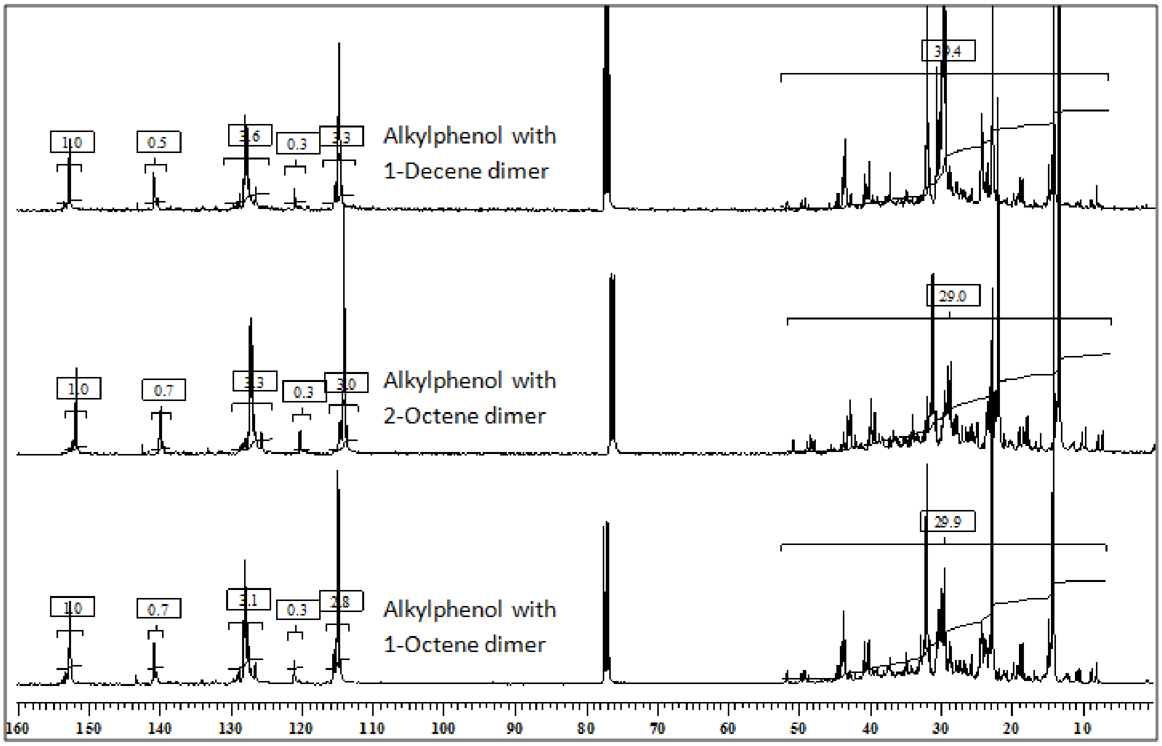


Figure 4.9: NMR results of pure alkyl phenols.

Chapter 5

Conclusions

In the present study dimerization reactions were studied for 2-Heptene, 1-Octene, 2-Octene, 1-Decene and Dodecene with different silica-alumina mole ratio Y-zeolites having H+ as nominal cation form. Among the zeolites, study was restricted to zeolite containing silica-alumina mole ratio of 5-80; the various zeolites studied were CBV 600, CBV 712(NH4+cation), CBV 712 (H+cation), CBV 720 and CBV 780. Among these the best results for dimerization were obtained with CBV 720.

Kinetics studies are performed for the various olefins studied and it was found that Octene gives the maximum rate in dimerization reaction as compared to 2-Heptene, 1-Decene and Dodecene. Among the Octenes, 2-Octene was found to have twice the rate of dimerization as compared to 1-Octene. Our interpretation to this behavior lies in the activity of olefin chains inside the zeolite catalyst. The rate controlling steps of dimerization reaction could be the rate of exit of product from the pores. Thus 2-Octene which forms dimers with lesser space volume as compared to 1-Octene dimers can exit faster from the pores of zeolite thus making their dimerizations faster. This fact is further exhibited by the rate of dimerization becoming slower on going to higher olefins like 1-decene and 1-dodecene.

To understand the detailed structure of the dimerized products structural characterization with ^{13}C NMR were carried out and their subsequent reactivity studied toward alkylation of phenol. The ratio of ortho to para isomers of the alkylphenol was found to be about 11% for 1-Octene dimer, 10% for 2-Octene dimer and about 9% for 1-Decene dimer. This implies that the steric factor around the olefinic double bond is highest for 1-Decene dimer followed by 2-Octene dimer and lastly for 1-Octene dimer as expected.

Chapter 6

Future scope of the thesis

This work belongs to a very wide field of research which can be taken to new levels in further studies:-

- Various other Olefins and their isomers can be studied to understand the reactivity sequence better.
- Reactivity pattern of the dimers towards other reactions can also be studied. This will help in further understanding these dimers structurally and also towards value generation from these dimers.

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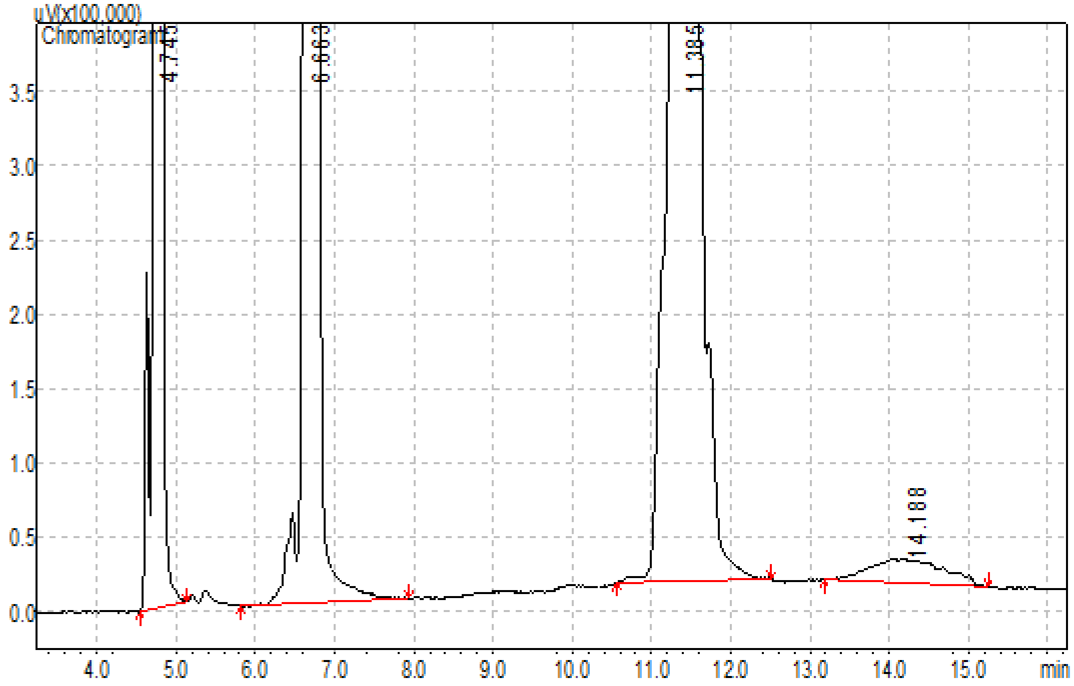
Appendices

Appendix 1

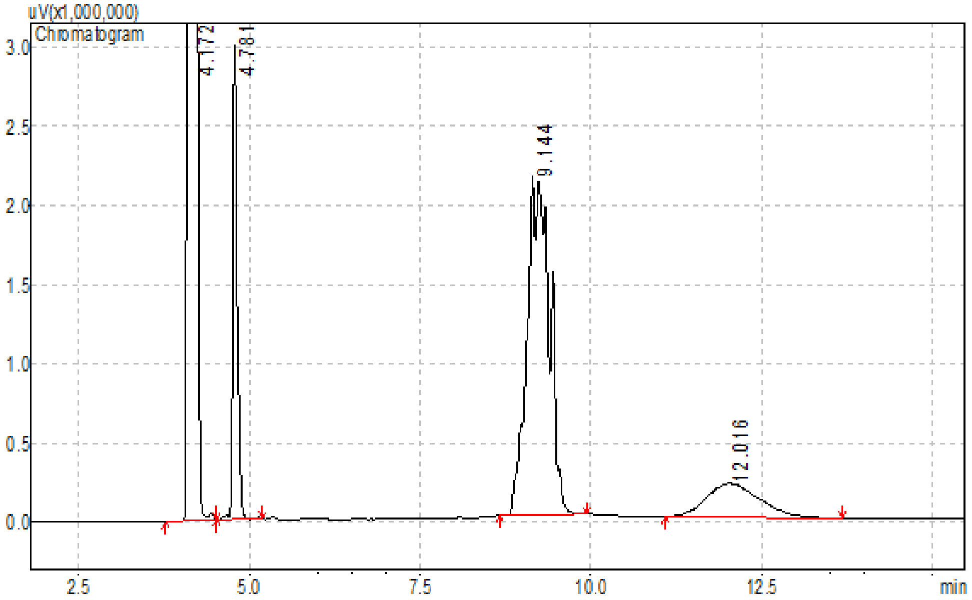
a) Chromatogram of 1-Decene dimerization reaction

At retention time 4.2-4.7 miutes a sharp peak of solvent i.e. n-hexane is observed, un-reacted 1-Decene peak is observed at a retention time of 6.5-6.6 minutes, the product dimer peak is obtained at 11.3-11.4 minutes and trimer can be seen at 14.0-14.3 minutes. The program is run for 30 min. but no further peaks of higher oligomer was observed.



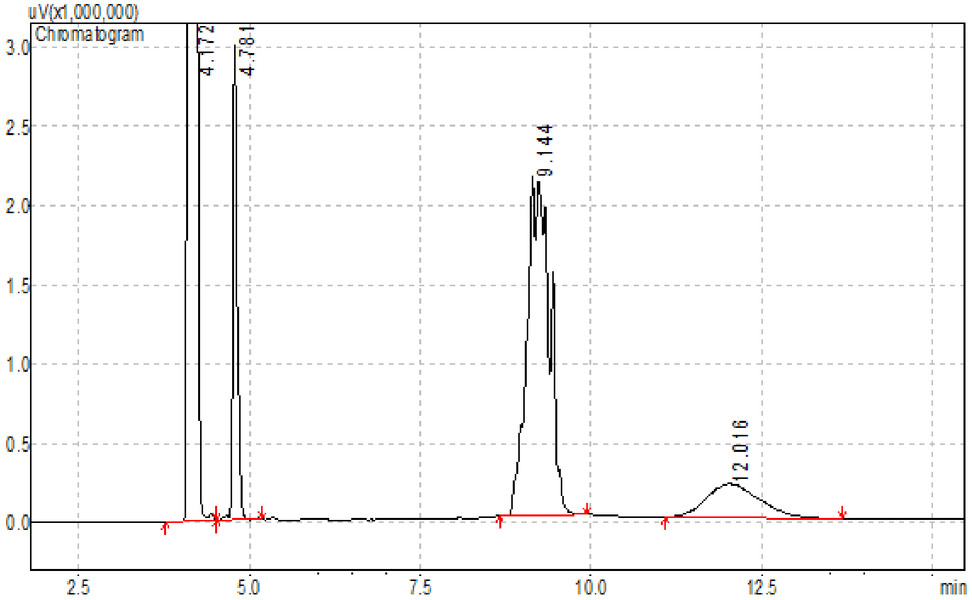
b) Chromatogram of 1-Octene dimerization reaction

At retention time 4.2-4.7 miutes a sharp peak of solvent i.e. n-hexane is observed, un-reacted 1-Octene peak is observed at a retention time of 4.7-4.86 minutes, the product dimer peak is obtained at 9.1-9.26 minutes and trimer can be seen at 12.0-12.51 minutes. The program is run for 30 min. but no further peaks of higher oligomer was observed.



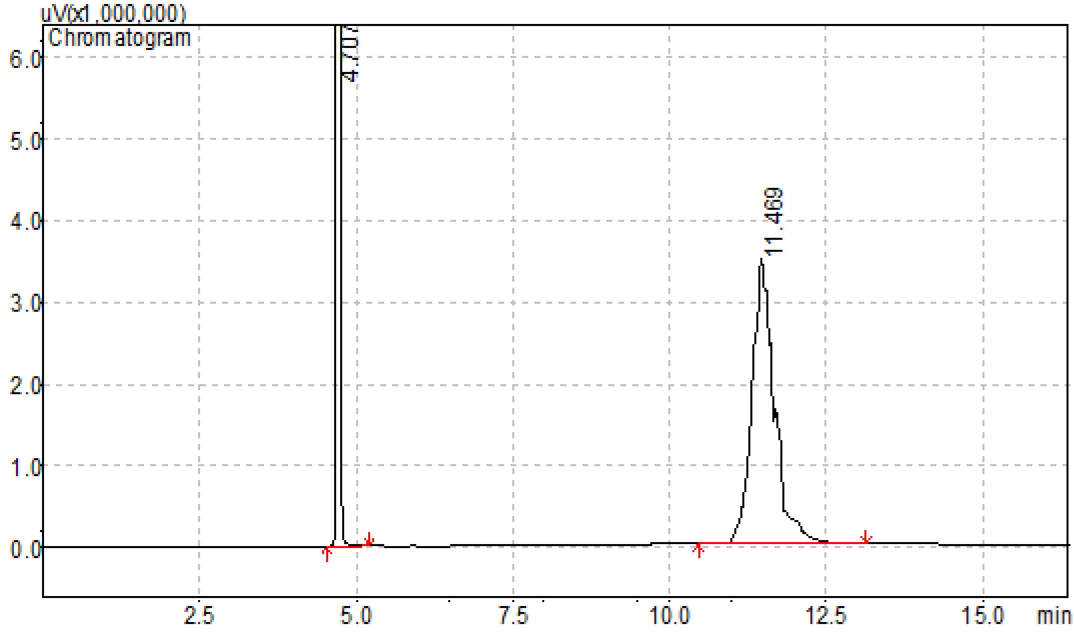
c) Chromatogram of 2-Octene dimerization reaction

At retention time 4.2-4.7 miutes a sharp peak of solvent i.e. n-hexane is observed, un-reacted 2-Octene peak is observed at a retention time of 4.7-4.9 minutes, the product dimer peak is obtained at 9.1-9.3 minutes and trimer can be seen at 12.0-12.1 minutes. The program is run for 30 min. but no further peaks of higher oligomer was observed.



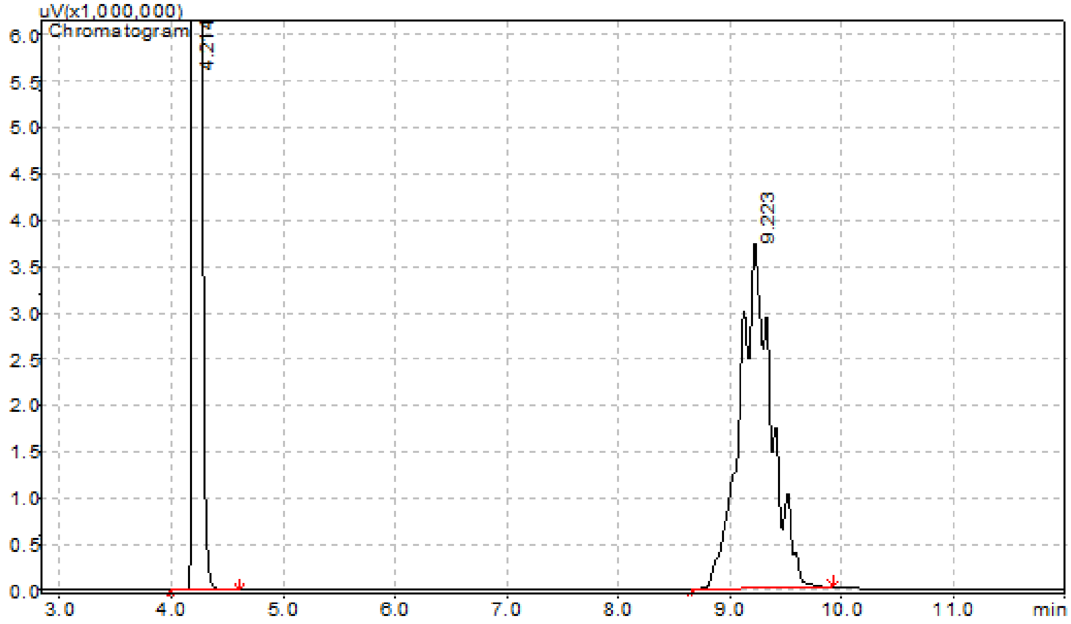
d) Chromatogram of pure 1-Decene dimer

To obtain pure dimer, distillation of reaction mixture is done. Firstly unreacted 1-Decene is seperated at 50 torr pressure and 130ºC temperature condition in a vaccuum distillation unit. Later dimer of 1-Decene is distilled out at 10 torr and 165-190ºC. The higher oligomers remain in the residue while the pure dimer is collected as distillate.



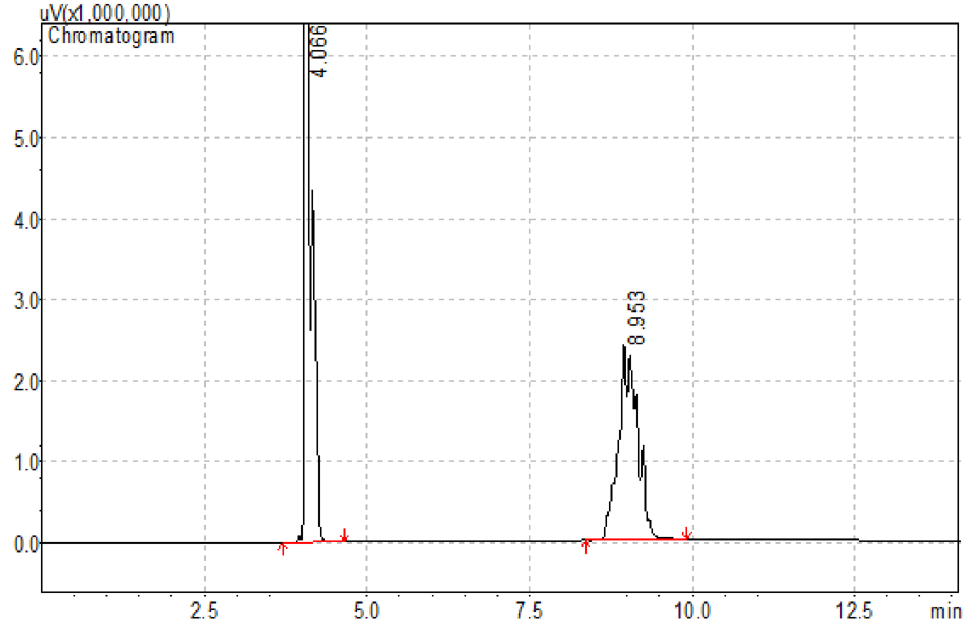
e) Chromatogram of pure 1-Octene dimer

To obtain pure dimer, distillation of reaction mixture is done. Firstly unreacted 1-Octene is seperated at 100 torr pressure and 65-80ºC temperature condition in a vaccuum distillation unit. Later 1-Octene dimer is distilled out at 10-8.7 torr and 130-143ºC. The higher oligomers remain in the residue while the pure dimer is collected as distillate.



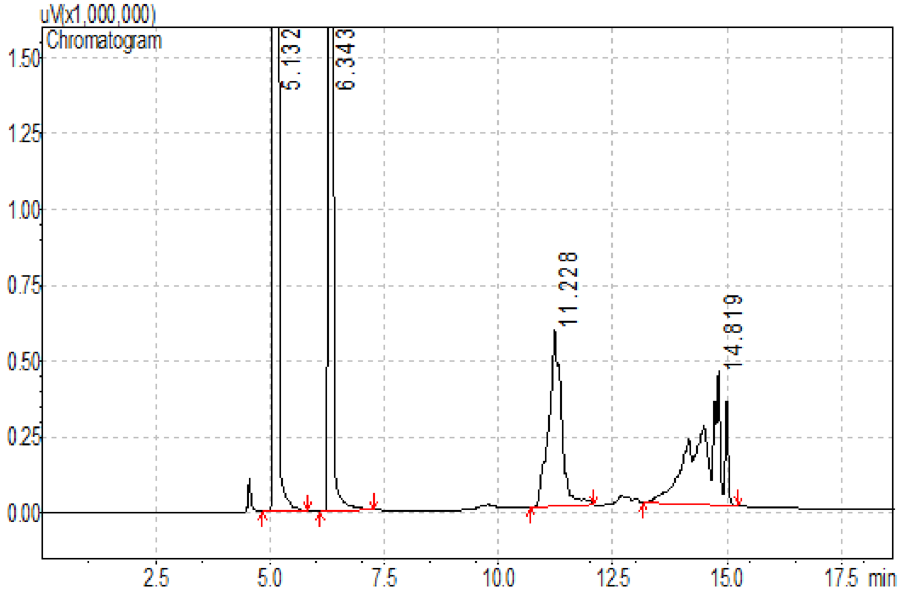
f) Chromatogram of pure 2-Octene dimer

To obtain pure dimer, distillation of reaction mixture is done. Firstly unreacted 2-Octene is seperated at 25-50 torr pressure and 75-100ºC temperature condition in a vaccuum distillation unit. Later 2-Octene dimer is distilled out at 10-8.7 torr and 149-178ºC. The higher oligomers remain in the residue while the pure dimer is collected as distillate.



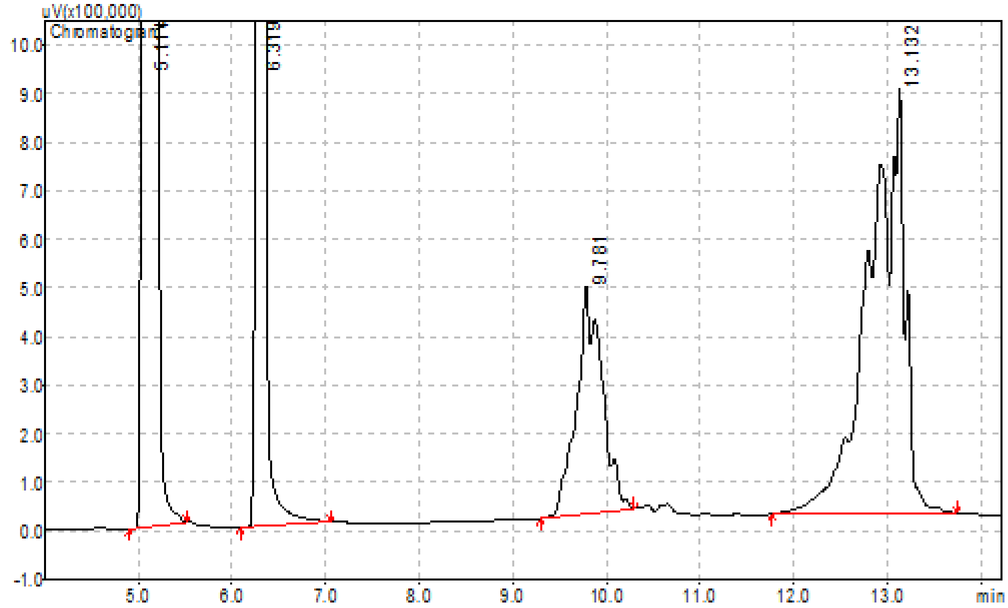
g) Chromatogram of Alkylation of phenol with 1-Decene dimer.

At retention time 5.1-6.2 miutes a sharp peak of solvent i.e. toluene is observed, un-reacted phenol peak is observed at a retention time of 6.5-6.6 minutes and 1-Decene dimer peak is obtained at 11.3-11.4 minutes. The product alkylphenol is obtained at 14.8-15.1 minutes. The program is run for 30 min. but no peaks were observed further.



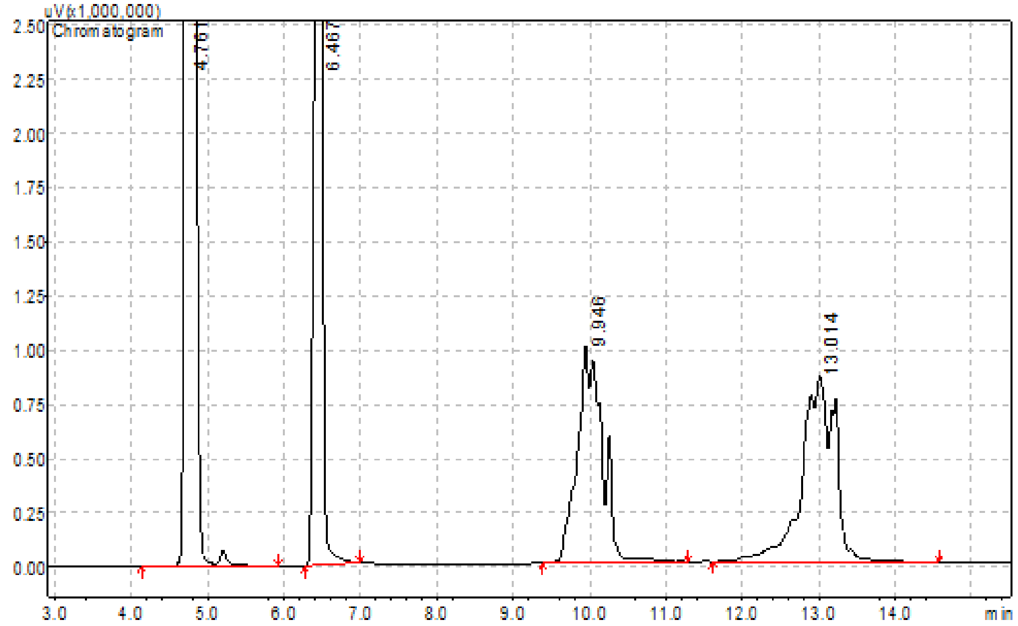
h) Chromatogram of Alkylation of phenol with 1-Octene dimer.

At retention time 5.1-6.2 miutes a sharp peak of solvent i.e. toluene is observed, un-reacted phenol peak is observed at a retention time of 6.5-6.6 minutes and 1-Octene dimer peak is obtained at 9.7-9.9 minutes. The product alkylphenol is obtained at 13.1 minutes. The program is run for 30 min. but no peaks were observed further.



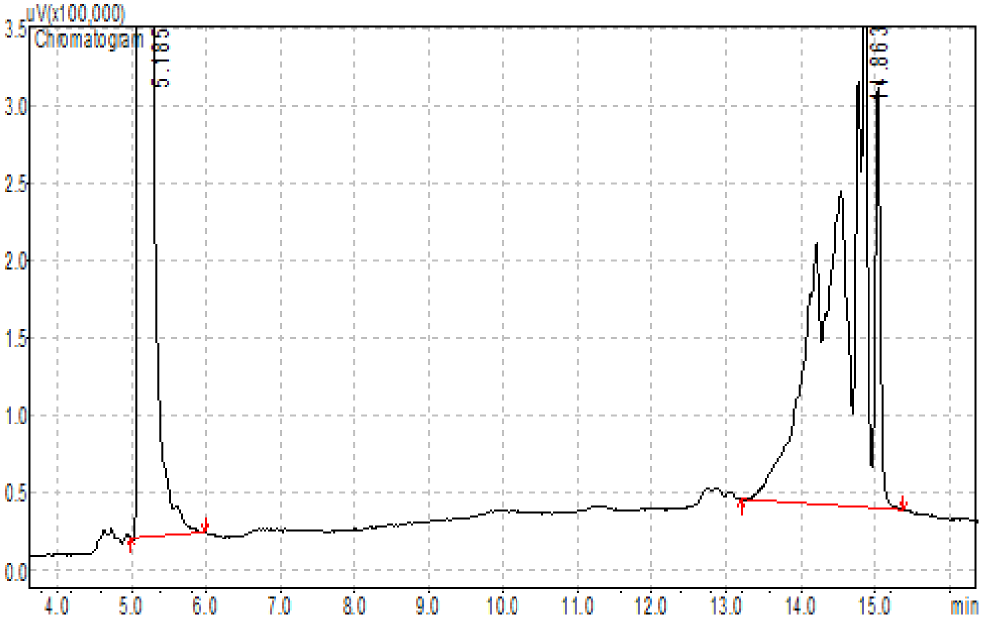
i) Chromatogram of Alkylation of phenol with 2-Octene dimer.

At retention time 5.1-6.2 miutes a sharp peak of solvent i.e. toluene is observed, un-reacted phenol peak is observed at a retention time of 6.5-6.6 minutes and 2-Octene dimer peak is obtained at 9.8-9.9 minutes. The product alkylphenol is obtained at 12.9-13.1 minutes. The program is run for 30 min. but no peaks were observed further.



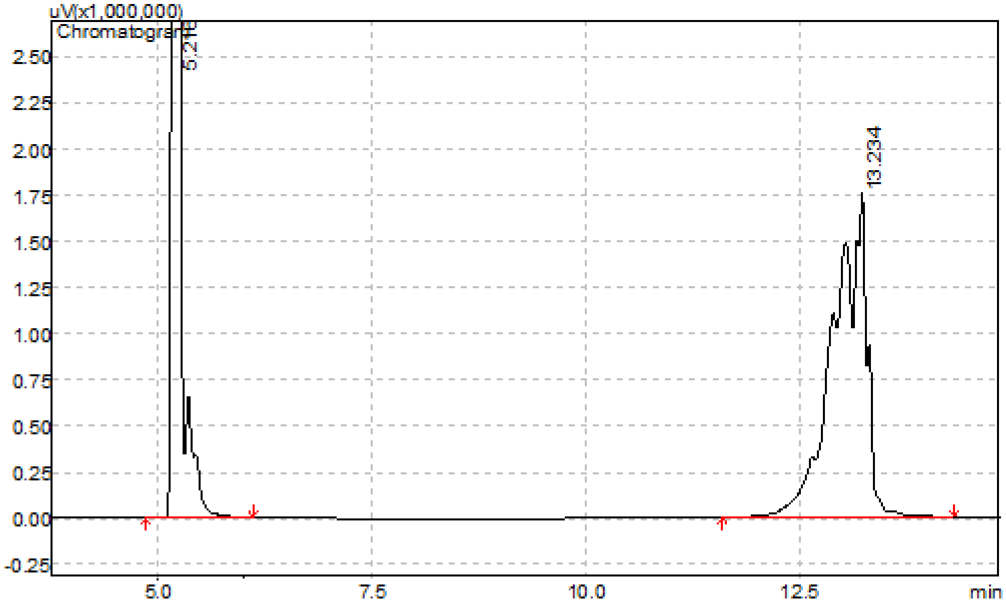
j) Chromatogram of pure 1-Decene Alkylphenol.

To obtain alkylphenol, distillation of reaction mixture is done. Firstly unreacted phenol is seperated at 60-44 torr and 90-117ºC pressure and temperature condition respectively in a vaccuum distillation unit. Later 1-Decene dimer is seperated at 10 torr and 165-190ºC. The pure alkylphenol remains as residue as all other impurities are separated out in distillates.



k) Chromatogram of pure 1-Octene Alkylphenol.

To obtain alkylphenol, distillation of reaction mixture is done. Firstly unreacted phenol is seperated at 60-44 torr and 90-117ºC pressure and temperature condition respectively in a vaccuum distillation unit. Later 1-Octene dimer is seperated at 10-8.7 torr and 130-143ºC. The pure alkylphenol remains as residue as all other impurities are separated out in distillates.



l) Chromatogram of pure 2-Octene Alkylphenol.

To obtain alkylphenol, distillation of reaction mixture is done. Firstly unreacted phenol is seperated at 60-44 torr and 90-117ºC pressure and temperature condition respectively in a vaccuum distillation unit. Later 1-Octene dimer is seperated at 10-8.7 torr and 130-143ºC. The pure alkylphenol remains as residue as all other impurities are separated out in distillates.