Chapter 4

Friedel-Crafts alkylation of 2-naphthol using Ionic Liquid as Catalyst
4.1 Introduction

2-naphthol or β-naphthol is a colourless crystalline solid with the formula C_{10}H_{7}OH. It is an isomer of 1-naphthol differing by the location of the hydroxyl group on naphthalene. The naphthols are naphthalene homologues of phenol, with the hydroxyl group being more reactive than in the phenols. Both isomers are soluble in simple alcohols, ethers and chloroform. They can be used in the production of dyes and in the organic synthesis.

Naphthols are the most important naphthalene derivatives as they are key intermediates in the production of many chemicals other than dyes and pigments. World production is estimated at 40,000 tpa of 1-naphthol and 1, 00,000 tpa of 2-naphthol. Naphthols resembles phenol in their chemical properties, but their hydroxyl groups are more reactive as explained by Elvers et al in 5th edition of Ullmann’s Encyclopaedia of Industrial Chemistry (1991), vol. A. 17, 15. Alkylated naphthols are key intermediates for dyes and other colourant applications.

After more than 125 years, the Friedel–Crafts alkylation is still one of the most studied and most utilised reactions in organic synthesis. Secret behind it is the great versatility in scope and applicability continues to justify its crucial role in the synthesis of more and more complex molecules. Herein we review use of Ionic liquid as catalyst in Friedel–Crafts alkylation reactions.

The Friedel–Crafts reaction is a very important process for C-C bond formation in organic chemistry. Various aromatic compounds, including benzenes with electro-donating substituents, furans, pyrroles, and indoles, have been applied successfully in a number of Friedel-Crafts reactions with diverse electrophiles. Enantioselective variants of this reaction have also been studied by Jensen et al. (2001) in the presence of chiral metal complexes. There are only a few reports on the Friedel–Crafts reaction of benzene derivatives bearing highly electron donating group as described by Zhao et al. (2006). Hence, there is need to developed novel Friedel–Crafts reaction, especially for electron rich arenes. Naphthol have been demonstrated to be good donors in Friedel-Crafts alkylation with a range of electrophiles, and various biologically active compounds and useful chiral ligands, for asymmetric catalysis can be prepared easily by this methods as explained by Erker et al.
Although Friedel–Crafts alkylations of naphthol derivatives with activated reagents such as iminium ions stated by Saidi and Aziz et al. (2003), α, β-unsaturated olefins by Kidwai et al. (2005) but very few work has been done on alkylation of 2-naphthol with tert-butyl alcohol.

The electronic structure of a molecule determines such physical and chemical properties as its charge distribution, geometry (and therefore the dipole moment), ionisation potential, electron affinity, and of course, chemical reactivity. If the electronic structure of a molecule were to be changed, one would expect its physical and chemical properties to be altered. Such a rearrangement can occur when a molecule is raised to an electronically excited state via the absorption of a quantum of light (i.e., a photon) whose energy matches the energy gap between the ground and excited states.

1 and 2 naphthols are interesting phenolic compounds that can be produced in 2 steps from naphthalene which is readily available in the form of moth balls. These 2 isomeric phenols are useful intermediates for the synthesis of catalysts, dyestuffs and quinone derivatives. The synthesis involves the sulphonation of naphthalene, isolation of the sulphonic acid as the sodium salt, fusion of the sodium sulphonate with potassium hydroxide and acidification of the fusion product to produce the crude product. The 2 isomers of the sulphonic acid can be produced by varying the temperature of the sulphonation reaction. Below 60 °C, the 1-sulphonic acid predominates, while at higher temperatures the 2-sulphonic acid predominates. This is an example of kinetic versus thermodynamic control of a chemical reaction. The 1-isomer is the kinetic product; it forms quicker at lower temperatures, while the 2-isomer is the thermodynamically more stable product and forms quickly at high temperatures.

One of the derivative of 6-tertbutynaphthol has found use as a powerful anthelmintic against tapeworm. Alkali salts are also used as detergents and the properties of its sodium salt have received pharmaceutical application as an ingredient in cough mixture as explained by Buu-Hoi et al. (1953).

The environment calls on the entire research community to define long terms strategic goals for clean chemistry and to reduce pollutants, especially organic solvents, whose recovery is
mandated by ever more strict law. To reduce the use of ecologically hazardous chemicals, it is advantages to carry out organic reaction in Ionic liquid media. It is recognised as an attractive medium for many organic reactions. Reactions in Ionic liquid are more environmental friendly, safe and simple to handle.
4.2 Conventional methods used

In 1887, Charles Friedel and James Mason Crafts isolated amylbenzene after the treatment of amyl chloride with AlCl₃ in benzene. This was not only one of the first descriptions of a Lewis acid used in organic synthesis but also the first example of what was later to be called Friedel-Crafts alkylation (FC alkylation) after its inventors. Today Friedel-Crafts alkylations remain the method of choice for the alkylation of arenes and heteroarenes.

The development of efficient Friedel-Crafts alkylations of arenes and heteroarenes using only catalytic amounts of a Lewis acid has gained much attention over the last decade. The new catalytic approaches described in this review are favoured over classical Friedel-Crafts conditions as benzyl-, propargyl-, and allyl alcohols, or styrenes, can be used instead of toxic benzyl halides. Additionally, only low catalyst loadings are needed to provide a wide range of products.

Furthermore, strong Brönsted acids including sulphuric acid, hydrofluoric acid or super acids such as HF•SbF₅ and HSO₃F•SbF₅ have also been shown to accelerate this transformation. Despite the great importance of the Friedel-Crafts alkylation for organic synthesis it has major drawbacks since stoichiometric or super stoichiometric amounts of a Lewis acid or Brönsted acid and toxic alkyl halides have to be utilised leading to vast amounts of salt side products. With the need for more environmentally and economically benign processes, the development of FC reactions using only catalytic amounts of a metal or acid catalyst would be highly desirable. In addition, the substitution of the alkyl chlorides by other, less toxic, alkylating reagents such as alcohols would be a major improvement as water would be the only side product. Beyond this, the use of activated double bonds and styrenes would be even more efficient as no side products are to be expected. However, good ideas always need time to develop and grow and thus it is not surprising that it took more than 100 years from the initial invention of Friedel and Crafts in 1887 until the first catalytic FC alkylations with alcohols and styrenes as alkylating reagents were developed. Initial attempts in 1996 using Sc(OTf)₃ and soon after with Mo(CO)₆ as Lewis acid catalysts were consequently followed by a multitude of new methods employing a variety of Lewis and Brönsted acid.
With regard to the electrophiles employed in the FC alkylation protected or activated alcohols and styrenes have been found to be suitable alkylating reagents giving access to many functionalised arenes including 1,1-diarylalkanes, allyl- and prop-2-ynyl-benzenes. More recently diastereoselective and enantioselective Friedel-Crafts alkylations have been developed. In this review we intend to give an overview of the important developments that have primarily emerged over the last decade.

The attempts carried out so far concerning catalytic of naphthols with alcohols have, as a rule brought about a complex mixture of products from which the separation of individual compounds with the aim of their practical utilisation has been proved to be impossible. We have found that naphthols and some of their derivatives could be easily alkylated with methanol or higher alcohols in the presence of iron oxide catalyst by a gas phase continuous process. As a result of alkylation the alkyl group enters into the ortho position to the hydroxyl group. The yields of alkylnaphthol are approximately about 90%, which simplifies their separation and purification considerably. The advantage of the newly developed method of alkylation is that it leads to high degree of raw material utilisation: it is practically waste less, thus it is well studied to the requirements of modern process technologies. It application may contribute to the increase of the demand for naphthol derivatives as potential raw material for many new syntheses of pharmaceuticals, plant protection agents, dyes etc.

The use of acid catalysts is very widespread in the chemical and allied industry and several reactions, such as Friedel–Crafts alkylation and acylation, isomerisation, esterification, etherification, hydration, dehydration, and nitration, employ liquid acids as catalysts which are corrosive and hazardous and present effluent treatment problems. They are typically neutralised with alkalis and thus cannot be reused. The overall process also becomes expensive and environmentally undesirable. Alkylated benzenes, which are produced by acid catalysed processes, are very valuable precursor in variety of industries such as bulk chemicals, fine chemicals, specialties etc. The conventional method of preparation of these alkyl aromatics is the homogeneous catalysed Friedel–Crafts reaction of olefins, halides and alcohols using Lewis acids (AlCl₃, FeCl₃, BF₃, ZnCl₂, TiCl₄, ZrCl₄) or Brønsted acids
polyphosphoric acid, sulphuric acid, hydrochloric acid, HF reported by Olah and Cupas (1966). For this purpose, the catalyst has to be employed in quantities over stoichiometric proportion of the reagent. Pressure from legislative and environmental bodies together with a growing awareness within the chemical industry has led to a search for new ecofriendly processes to replace unacceptable out dated reactions. To make the process that could be environmentally benign and also inexpensive.
4.3 Literature Survey

Halimehjani et al. (2009) proposed the accelerated Michael-type Friedel–Crafts alkylation of naphthols with nitrostyrenes in the presence of water is reported. The procedure is simple and catalyst free to give good yield of products.

Wrzyszcz et al. (1997) observed that alkyl group enters into the ortho position to the hydroxyl group in presence of iron oxide catalyst by a gas phase continuous process. The yields of alkylnaphthols are 90%, which simplifies their separation and purification considerably.

Layer (1974) found that 3 position of 2-naphthol is much more reactive than previously thought, 3-tertbutyl-2-naphthol is formed, as well as 6-tertbutyl-2-naphthol, during the butylation of 2-naphthol with isobutylene using p-toluenesulphonic acid as catalyst at 110°C.

Brady et al. (1972) proved that the dialkylated derivative can be formed by the mono-derivative by further alkylation. Which was further accepted and even supported by later workers on the basis of the long half life of a derived radical or radicals of unknown structure.

Earle et al. (1998) carried out alkylation of 2-naphthol using alkyl halide as an alkylating agent and Ionic liquid [bmim] [PF₆] is use as an alternative to dipolar aprotic solvents for regioselective alkylation.

Li et al. (2007) studied the alkylation of 2-naphthol with tripropylene in the presence of zeolite catalyst H-BEA and H-MFI. It was found that he structure and acid strength of zeolite were major influencing factors for the conversion and selectivity of 2-naphthol alkylation.

Grabowska et al. (1997) carried out vapour phase alkylation of 2-naphthol with C1-C3 alcohols in the presence of an iron catalyst contains Cr, Si and K oxides. In case of ethanol and n-propanol derivatives of 2-naphthol alkylated in the 1 position obtained with high yield and selectivity. The reactions were carried out in a continuous process at atmospheric pressure.
4.4 Experimental Data

4.4.1 Material and Reagents

Crystalline 2-naphthol and Diethyl ether were purchased from S. D. fine-chem. Limited, Mumbai. Tertiary butyl alcohol was purchased from Central Drug House Pvt. Ltd., New Delhi. 1, 4-butanesultone and p-toluenesulphonic acid were purchased from Merck India Ltd. (Mumbai, Maharashtra, India), while triethylamine was purchased from Thomas Baker (chemicals) Pvt. Ltd. The ionic liquid [BMIM] [HSO4], [BMIM] [PTSA], and [TTDP] [HSO4] used in reaction were synthesised in laboratory. All other chemicals were obtained from reputed firms. They were used without further purification.

4.4.2 Synthesis of Ionic Liquid

4.4.2.1 1-butyl 3-methylimidazolium para-toluenesulphonic acid ([BMIM][PTSA–])

1-Butyl 3-methylimidazolium chloride (1.74 g, 0.01 mol) was placed in a two necked flask with stirrer and was cooled to 0°C. Then 5ml of water was added to it and para-toluene sulphonic acid (1.90 g, 0.01 mol) was added slowly under stirring. The mixture was stirred for 2 h, and the water was removed on a rota-evaporator at 60°C to obtain a green colour liquid as the procedure explain by Joseph et al. (2005).

![Figure 4.1 structure of [BMIM] [PTSA]](image)

Figure 4.1 structure of [BMIM] [PTSA]
4.4.2.2 1-Butyl 3-Methyl Imidazolium Hydrogen Sulphate (BMIM [HSO₄])

[BMIM][Cl] (25gm) and KHSO₄ (19.48gm) was added in 1:1 proportion and methanol was used as a solvent (20 ml) in three necked stirred reactor. The mixture was stirred for 30 hrs at 650 rpm. After that the precipitate of KCL formed was filtered and dried in rota-evaporator at 60°C, for 2hrs as explained by Joseph et al. (2005).

![Figure 4.2 Structure of [BMIM] [HSO₄]](image)

4.4.2.3 Trihexyl (tetradecyl) phosphonium hydrogen sulphate. [TTDP][HSO₄]

By combining trihexyl (tetradecyl)phosphonium chloride (0.66 kg, 1.26 mol, Cytec Industries) and sulphuric acid (0.2348gm) in the presence of an excess of sodium hydroxide (40% w/w in water, 0.24 kg, 2.43 mol) an water. This mixture was heated to 55 °C with vigorous agitation for 4 h, and washed three times with water to remove sodium chloride. Vacuum stripping at 135 °C to remove any residual water gave the product, an orange/brown liquid, in 95% isolated yield (0.93 kg, 1.20 mol, chloride content 0.082% w/w by titration with AgNO₃) followed the procedure as stated by Bradaric et al. (2002).
4.4.2.4. (1-(4-sulphonic acid) butyl triethylammonium p-toluene sulphonic acid

[SBTEA][PTSA]

Triethylamine was mixed with 1,4- butane sultone and stirred at 333 K for 24 h. After solidification of the mass, the product (zwitterion) was washed three times with methanol and ethyl acetate and then dried under a vacuum (353 K, 0.01 Torr). A stoichiometric amount of sulphuric acid or p-toluene sulphonic acid was added to the precursor zwitterion. The mixture was stirred at 353 K for 8 h to form the ionic liquid. The product phase was washed with solvent and dried in a Vacuum (Nie et al., 2010).
4.4.3 Experimental set-up

The reactions were carried out in three necks round bottom flask with magnetic needle. The overall capacity of round bottom flask was 25 ml. It was provided with condenser and temperature thermometer to measure the temperature. The speed of agitation and temperature of reaction mixture in round bottom flask was controlled by Digital magnetic stirrer. The figure 4.5 shows the assembly of reaction set up.

Figure 4.5 Experimental setup
4.4.4 Experimental Procedure

6. The required amount of ionic liquid is weight and added in 25 ml three necked Round bottom flask.

7. Required volume of 2-naphthol and tertiary butyl alcohol is added to Round bottom flask containing ionic liquid.

8. The reaction mixture is heated to 70°C with continuous stirring for 6 hr.

9. The Sample is analysed using gas chromatography.

4.4.5 Analysis

The analysis is done using High Performance Liquid Chromatography (HPLC) with Reverse phase C18 Column using UV detector. Acetonitrile:Ethanol 70:30 ratio, at flow rate of 0.5 ml/min.
4.4.6 Mechanism of the Reaction

Schematic representation of the reaction

Alkylation Reaction of 2-naphthol with tert-butyl alcohol

Figure 4.6: Alkylation reaction of 2-naphthol with Tertiary butyl alcohol

Figure (4.6) shows the alkylation reaction of 2-naphthol with Tertiary butyl alcohol (TBA). The products of the reaction are 3-tertiarybutynaphthol, 6-tertiarybutynaphthol, 3,6-diteriarybutynaphthol and water. The above mentioned products formed in the presence of (1-(4-sulphonic acid) butyl triethylammonium p-toluene sulphonic acid [SBTEA][HSO₄]) as a catalyst.
4.4.8 Mechanism of alkylation reaction using ionic liquid as a catalyst:

Step 1: Ionic liquid donates its proton to tertiary butyl to form tertiary butyl cation with the removal of water molecule.

Step 2: This cation attack the various position of 2-naphthol ring to form products.

Step 3: Hydrogen gets released when cation attacks 2-naphthol ring at various positions which again combine with ionic liquid.
[IL]: Ionic liquid.
4.6 Results and Discussion

The alkylation reaction of 2-naphthol with tertiary butyl alcohol was studied using four different ionic liquids. Different ionic liquids were 1-butyl 3-methylimidazolium para-toluenesulphonic acid ([BMIM][PTSA]), 1-Butyl 3-Methyl Imidazolium hydrogen sulphate (BMIM [HSO₄]), and trihexyl (tetradecyl) phosphonium hydrogen sulphate. [TTDP][HSO₄], and (1-(4-sulphonic acid) butyl triethylammonium p-toluene sulphonic acid [SBTEA][PTSA]. The reaction was studied at parameters mentioned in Table 4.1. Less conversion of 2-naphthol was obtained when 1-butyl 3-methylimidazolium para-toluenesulphonic acid ([BMIM][PTSA], 1-Butyl 3-Methyl Imidazolium hydrogen sulphate [BMIM][HSO₄] and Trihexyl(tetradecyl) phosphonium hydrogen sulphate. [TTDP][HSO₄] ionic liquids were used as catalyst. While (1-(4-sulphonic acid) butyl triethylammonium p-toluene sulphonic acid [SBTEA][PTSA] gave good conversion so all further experiments were carried out using this ionic liquid only.

Table 4.1: Parameter studied at atmosphere pressure with their range for 2-naphthol reactions.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Parameters</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Speed of agitation (rev/min)</td>
<td>300 – 1000 rpm</td>
</tr>
<tr>
<td>2</td>
<td>Reaction Temperature</td>
<td>323 – 343°K</td>
</tr>
<tr>
<td>3</td>
<td>Change of Concentration of Reactant.</td>
<td>1:1 – 1:2ᵃ</td>
</tr>
<tr>
<td>4</td>
<td>Catalyst loading</td>
<td>1:0.1 – 1:0.5ᵇ</td>
</tr>
</tbody>
</table>

ᵃ: ratio of moles of 2-naphthol to TBA.
ᵇ: ratio of moles of 2-naphthol to ILs.
4.6.1 Effect of speed of agitation

4.6.1 Conversion of 2-naphthol

Figure 4.7: Effect of speed of agitation on the conversion (Condition: 70°C, 2-naphthol/TBA 1:2 mol/mol, Catalyst loading 2-naphthol/ILs 1:0.5 mol/mol, 6 hr)

The reaction was carried out at temperature of 70°C, 1:2 molar ratio of 2-naphthol to Tertiary butyl alcohol and 1:0.5 molar ratio catalyst loading of 2-naphthol to Ionic liquid [SBTEA][PTSA]. The agitation speed increases from 200 rpm to 12000 rpm. Figure 4.7 shows the effect of speed of agitation on the conversion of 2-naphthol. It is clear that the maximum conversion of 2-naphthol obtained at 1000 rpm which is 85.2% remains constant for further increase in speed of agitations i.e. up to 12000rpm. Which depicts that after 1000rpm reaction is independent of mass transfer coefficient. Hence 1000rpm is considered to be constant speed of agitation of all experiments carried out.

4.6.2 Effect of Reaction Temperature
4.6.2.1 Conversion of Reactant

![Graph showing the effect of reaction temperature on the conversion of 2-naphthol.](image)

**Figure 4.8** Effect of reaction temperature on the conversion of 2-naphthol.

The Figure 4.8 shows the effect of Temperature on the conversion of 2-naphthol. The reaction was carried out at speed of agitation of 1000 rpm, 1:2 molar ratio of 2-naphthol to Tertiary butyl alcohol and 1:0.5 catalyst loading of 2-naphthol to Ionic liquid [SBTA][PTSA]. The reaction temperature was varied from 50°C to 70°C. The conversion continuously increases up to 6 hr, after that rate of conversion decreases. The maximum conversion obtained after 6 hr at 70°C. While the least conversion obtained after 6 hr at 70°C.
4.6.2.2 Conversion of % conversion of 3-tertbutynaphthol

Figure 4.9 Effect of reaction temperature on the conversion of 3-tertbutynaphthol.

Figure 4.9 illustrates the effect of reaction temperature on the conversion of 3-tertbutynaphthol. The reaction was carried out at speed of agitation of 1000 rpm, 1:2 molar ratio of 2-naphthol to Tertiary butyl alcohol and 1:0.5 catalyst loading of 2-naphthol to Ionic liquid [SBTEA][PTSA]. The reaction temperature was varied from 50°C to 70°C. Fig. 3.8.6 shows that increase in temperature results in decrease in the conversion of 3-tertbutynaphthol. The conversion of 3-tertbutynaphthol is less, due to Di-alkylation.
4.6.2.3 Conversion of 6-tertbutylnapthol

Figure 4.10: Effect of reaction temperature on the conversion of 6-tertbutylnapthol

Figure 4.10 depicts the effect of reaction temperature on conversion of 6-tertbutylnapthol. The reaction was carried out at speed of agitation of 1000 rpm, 1:2 molar ratio of 2-naphthol to Tertiary butyl alcohol and 1:0.5 catalyst loading of 2-naphthol to Ionic liquid [ESBTEA][PTSA]. The reaction temperature was varied from 50°C to 70°C. It is observed from the figure conversion of 6-tertbutylnapthol at 70°C is maximum at initial period of time where as it decreases with time since mono product further undergoes reaction to form dialkylated products.
4.6.2.4 Conversion of 3.6-ditertbutynaphthol

![Graph showing conversion of 3.6-ditertbutynaphthol at different temperatures]

**Figure 4.11:** Effect of reaction temperature on the Conversion of 3.6-ditertbutynaphthol

Figure 4.11 illustrate the effect of reaction temperature on the conversion of 3,6-ditertbutynaphthol. The reaction was carried out at speed of agitation of 1000 rpm, 1:2 molar ratio of 2-naphthol to Tertiary butyl alcohol and 1:0.5 catalyst loading of 2-naphthol to Ionic liquid [SABTEA][PTSA]. The reaction temperature was varied from 50°C to 70°C. From figure it is clear that the maximum conversion of 3,6-ditertbutynaphthol obtained at 70°C, while the conversion of 88.21% was observed at 70°C temperature, as compared to lower temperature since at low temperature the mono product formed at very less amount so further conversion of dialkylated product also decreases.
Conclusions:

From the experimental data, 70°C considered as the optimum temperature for the system because of the following reasons

4) Highest conversion to 2-naphthol.

5) Highest conversion of 3,6-ditertbutynaphthol

6) Highest dialkylation
4.6.3 Effect of change in concentration of Reactant.

4.6.3.1 Conversion of 2-naphthol

Figure 4.12 Effect of reactant concentration on conversion of 2-naphthol (Condition: 70°C, Catalyst loading 2-naphthol/ILs 1:1 mol/mol, 6 hr)

Figure 4.12 shows the effect of reactant concentration on the conversion of 2-naphthol. The reaction was carried out at speed of agitation of 1000 rpm, and 1:0.5 catalyst loading of 2-naphthol to ionic liquid [SBTEA][PTSA]. The reactant molar ratio of 2-naphthol to tertiary butyl alcohol was varied from 1:1 to 1:2. From the graph it is clear that as concentration of tertiary butyl alcohol increases from 1:1 to 1:2, the conversion of 2-naphthol increases. Thus the maximum conversion of 2-naphthol obtained at 1:2 ratio 2-naphthol to tertiary butyl alcohol is 97.12%.
4.6.3.2 Selectivity of Conversion of 3-tertbutynaphthol

![Graph showing the effect of reactant concentrations on conversion of 3-tertbutynaphthol.](image)

**Figure 4.13** Effect of reactants concentrations on conversion of 3-tertbutynaphthol.

Figure 4.13 shows the effect of concentration of reactant concentration on conversion of 3-tertbutynaphthol. The reaction was carried out at speed of agitation of 1000 rpm, and 1:0.5 catalyst loading of 2-naphthol to Ionic liquid [SBTEA][PTSA]. The reactant molar ratio of 2-naphthol to tertiary butyl alcohol was varied from 1:1 to 1:2. For the entire molar ratio it is observed that, conversion of 3-tertbutynaphthol decreases with the time. This is due to dialkylation of 3-tertbutynaphthol. The minimum conversion of 3-tertbutynaphthol observed at 2:1 molar ratio of 2-naphthol to TBA, while maximum conversion observed at 1:2 molar ratios.
4.6.3.3 Conversion of 6-tertbutynaphthol

The figure 4.14 shows the effect of reactant concentration on conversion of 6-tertbutynaphthol. The reaction was carried out at speed of agitation of 1000 rpm, and 1:0.5 catalyst loading of 2-naphthol to Ionic liquid [SBTEA][PTSA]. The reactant molar ratio of 2-naphthol to tertiary butyl alcohol was varied from 1:1 to 1:2. From the figure it is clear that the conversion of 6-tertbutynaphthol continuously decreases with time at all the reactant concentration. It happens due to dialkylation of mono-products. The maximum conversion of 6-tertbutynaphthol is observed at 1:2 molar ratio of 2-naphthol to TBA, while minimum selectivity observed at 2:1 molar ratio of 2-naphthol to TBA.
Figure 4.15 illustrates the Effect of reactant concentration on conversion of 3,6-diterbutyl-naphthol. The reaction was carried out at speed of agitation of 1000 rpm and 1:0.5 catalyst loading of 2-naphthol to Ionic liquid [SBTEA][PTSA]. The reactant molar ratio of 2-naphthol to tertiary butyl alcohol was varied from 1:1 to 1:2. From the figure it is clear that conversion of 3,6-diterbutyl-naphthol increases with time. The maximum conversion of 3,6-diterbutyl-naphthol was obtained at 1:2 molar ratio of 2-naphthol to TBA, while the minimum conversion was at 2:1 molar ratio of 2-naphthol to TBA.
Conclusions:

From the experiment conducted, 1:2 molar ratio of 2-naphthol to TBA considered as optimum molar ratio because of following reasons

5) Highest conversion of 2-naphthol

6) Maximum formation of 3,6-ditertbutylnapthol.

7) Highest dialkylation.

8) Minimum formation of monoalkylated products
4.6.4 Effect of catalyst loading

4.6.4.1 Conversion of 3-tertbutynaphthol

Figure 4.16: Effect of catalyst loading on conversion of 3-tertbutynaphthol.

Figure 4.16 shows the effect of Catalyst loading on conversion of 3-tertbutynaphthol. The reaction was carried out at speed of agitation of 1000 rpm, 1:2 molar ratio of 2-naphthol to Tertiary butyl alcohol and the temperature of 70°C. Catalyst loading of 2-naphthol to Ionic liquid [SBTEA][PTSA] was varied from 1:0.1 to 1:0.5. At all catalyst loading conversion of 3-tertbutynaphthol was found to decreases with time. The maximum conversion of 3-tertbutynaphthol obtained at 1:0.5 molar ratio of 2-naphthol to ionic liquid. Thus conversion is maximum at 1:0.5 molar ratio compare to other ratios.
4.6.4.2 Conversion of 6-tertbutynaphthol

![Graph showing the effect of catalyst loading on conversion of 6-tertbutynaphthol.](image)

**Figure 4.17** Effect of catalyst loading on conversion 6-tertbutynaphthol.

Figure 4.17 shows the effect of catalyst loading on conversion 6-tertbutynaphthol. The reaction was carried out at speed of agitation of 1000 rpm, 1:2 molar ratio of 2-naphthol to Tertiary butyl alcohol and the temperature of 70°C. Catalyst loading of 2-naphthol to Ionic liquid [SBTEA][PTSA] varied from 1:0.1 to 1:0.5. From the Figure it is clear that the conversion 6-tertbutynaphthol slowly increases with time at all catalyst loading, due to Di-alkylation of monoproduction. The conversion 6-tertbutynaphthol is maximum at 1:0.5 molar ratio of 2-naphthol to TBA.
4.6.4.3 Conversion of 3,6-ditertbutynaphthol

![Graph showing the effect of catalyst loading on conversion of 3,6-ditertbutynaphthol.]

**Figure 4.18** Effect of catalyst loading on conversion of 3,6-ditertbutynaphthol.

Figure 4.18 illustrates the effect of catalyst loading on conversion of 3,6-ditertbutynaphthol. The reaction was carried out at speed of agitation of 1000 rpm, 1:2 molar ratio of 2-naphthol to Tertiary butyl alcohol and the temperature of 70°C. Catalyst loading of 2-naphthol to Ionic liquid [SBTEA][PTSA] varied from 1:0.1 to 1:0.5. Figure shows that with time the conversion of 3,6-ditertbutynaphthol increases. The maximum conversion of 3,6-ditertbutynaphthol obtained at 1:0.5 molar ratio of 2-naphthol to ionic liquid, while the minimum selectivity obtained at 1:0.1 molar ratio of 2-naphthol to ionic liquid.
Conclusions:
From the experiment conducted, catalyst loading of 1:0.5 considered as optimum because of following reasons

4) Higher conversion of 2-naphthol

5) Highest conversion of 3,6-ditertbutylnaphthol.

6) Less formation of monoproduts
4.6.5 Catalyst reusability

In order to examine the recoverability and recyclability of the ionic liquid, after the reaction, the ionic liquid was extracted with water then dried under vacuum for 5 h. After vacuum drying, IL was repeatedly used 4 times without any significant decrease in 2-naphthol conversion as well as desired product selectivity is also not been affected much, as shown in Table 4.2

<table>
<thead>
<tr>
<th>Experimental run</th>
<th>Conversion of 2-naphthol (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh catalyst</td>
<td>97.1</td>
<td>5.55 6.9 88.91</td>
</tr>
<tr>
<td>Recycle 1</td>
<td>96.39</td>
<td>5.15 6.10 87.14</td>
</tr>
<tr>
<td>Recycle 2</td>
<td>95.29</td>
<td>5.22 6.3 86.31</td>
</tr>
<tr>
<td>Recycle 3</td>
<td>95.12</td>
<td>5.10 5.81 81.46</td>
</tr>
<tr>
<td>Recycle 4</td>
<td>93.67</td>
<td>4.8 5.80 77.46</td>
</tr>
</tbody>
</table>
4.7 Conclusions

- Better conversion of 3,6-ditertbutynapthathol is observed using laboratory synthesised IL (1-(4-sulphonic acid) butyl triethylammonium \( p \)-toluene sulphonic acid.
- Reaction occurs at mild acidic condition and lower temperature at 70°C.
- Dialkylated product i.e. 3,6-ditertbutynapathol is selectively formed in higher concentration as compared to mono-products.
- Optimum condition is at 70°C, 1:2:0.5 molar ration of Phenol: TBA: IL, 6 hr.
- Reaction is pseudo 2\(^{nd}\) order with respect to naphthol and TBA.