

The effect of solvents on the conversion of oxidative coupling of 2-naphthol by reciprocating reactor

Pariya Noeparvar*, Jafar Sadegh Moghaddas, Naimeh Jodeiri, Hani Taleshi Ahangari
Chemical Engineering Faculty Transport Phenomena Research Centre, Sahand University of Technology, Tabriz, (IRAN)
E-mail: paria1219@gmail.com

ABSTRACT

In this study, a kind of ball mill called reciprocating reactor were studied. Furthermore, methods of production of binaphthol from oxidative coupling reaction of 2-naphthol were classified by reciprocating reactor; moreover, oxidative coupling reaction of 2-naphthol in presence of Iron (III) Chloride Hexahydrate as catalyst with chlorobenzane, 1,2-dichloroethane, chloroform and water as solvents were investigated to produce binaphthol. Consequently, performing this reaction in reciprocating reactor with different solvents should be taken into account as a novel work and no similar research has been done previously.

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KEYWORDS

Catalyst;
Oxidative reaction;
Reciprocating reactor;
Solvent;
2-Naphthol.

INTRODUCTION

Ball milling has been the subject of multitudinous research in the last past decade. Reduction in size of the process with a focus on reducing energy consumption is presented. In fact, a great deal of energy is required to break particles; however, the size reduction is needed to avoid excess grinding energy consumption^[1]. Reciprocating machines, which should be taken into account as a kind of ball mill, are used for milling to produce fine particles, mostly in the cement industry, mining and functional units^[2-4]. These machines represent a useful tool for mixing where yield is high^[5]. High conversion mixings, which requires continuous contacts between the imaging modalities reactions especially in response to the solid–solid system, might apparently be significant. Milling with a new place to call would be more effective in comparison with grinding^[6]. In reciprocating machines, raw materials are put between the surfaces and pressed together. This compression is due to frictional forces which are generated in collisions. In

synthesis of chemicals, reciprocating machines improve reaction conditions and reactivity; what is more, it should be stated that the mechanical activation could surprisingly be grown up^[7].

Oxidative coupling of 2-naphthol eventuate in important compound of 1-1'-bi-2-naphthol (binaphthol) which is used as an organic synthesis of chiral^[8]. Naphthols are widely applied for synthesis of several kinds of dyes, pigments, fluorescent whitening agents, substances used in tanning and as a raw material for the manufacture of certain drugs, antioxidants and pesticides^[9]. Moreover, the use of chiral binaphthol for the production of *enantioselective* catalyst promotes a variety of reactions in homogenous systems^[10-13]. In this study, oxidative coupling reaction of 2-naphthol as a type of solid–solid reaction in presence of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, with chlorobenzane, 1,2-dichloroethane, chloroform and water as solvent was examined by reciprocating reactor to produce binaphthol with high yield.

Sharma et al. studied oxidative coupling reaction of 2-naphthol complex in presence of catalyst Schiff base

copper (II). They used chlorobenzene, acetonitrile, 1,2-dichloroethane and toluene as solvents to assess the effect of such solvents. It was proposed that the rate of oxidative coupling of 2-naphthol is very low at room temperature and can have high yield with refluxed chlorobenzene^[14]. In another study, Sharma et al. examined oxidative coupling reaction of 2-naphthol in presence of MTO (Methyltrioxorhenium) as catalyst and by using molecular oxygen in the role of oxidizing. Reaction yields at best condition were found 95% in 10 hours^[15].

Habaue et al. performed oxidative coupling reaction of 2-naphthol with methyl-3-hydroxy-2-naphthoate as solvent in presence of CuCl(OH)-TMEDA (copper(II)-tetramethylethylenediamine) as catalyst in THF (Tetrahydrofuran) solvent at room temperature and under atmospheric oxygen in the presence and in the absence of Yb(OTf)₃ (Ytterbium (III) trifluoromethanesulfonate). They achieved 91% yields in 36 hours^[16].

Li Chen et al. provided a method for oxidative coupling of 2-naphthol by using different solvents in the presence of catalyst Cu (I or II)-N-alkylimidazole and found different values for the yields of binaphthol. Dichloromethane, methanol, acetone and ethyl acetate were tested as solvent that dichloromethane was found the best of all^[17].

Ikeda et al. performed oxidative coupling reaction of 2-naphthol with dichloromethane as solvent in the liquid phase and in presence of vanadium impregnated catalysts based on inorganic oxides such as MCM-41 (Mobil Catalytic Material Number 41), using molecular oxygen as the oxidant. TABLE 1 shows a comparison of different solvents on oxidative coupling reaction of 2-naphthol^[18].

Eshghi et al. evaluated oxidative coupling reaction of 2-naphthol with the Ferric Hydrogen Sulfate as cata-

lyst, in water and under solvent-free conditions. Oxidative coupling of 2-naphthol is extremely weak at low temperatures and will have best conversion with boiling water by approximately 98%. Moreover, this reaction has 95% conversion under solvent-free conditions using SFHS (Ferric Hydrogen Sulfate supported on Silica) at 90°C^[19].

EXPERIMENTAL

Materials

The information and applications of required materials to carry out the reaction and also to identify the product are listed in TABLE 2.

All reactions were carried out in a reciprocating reactor located in Transport Phenomena Centre of Sahand University of Technology in Tabriz, Iran. Infrared spectra were taken by a Mattson 1000 FTIR instrument.

TABLE 2 : Materials for binaphthol production

Materials	Chemical formula	Application	Manufacturer
2-naphthol	C ₁₀ H ₈ O	raw material	Merk
Iron (III) Chloride Hexahydrate	FeCl ₃ .6H ₂ O	oxidizing agent	Merk
Chlorobenzene	C ₆ H ₅ Cl	solvent	Merk
1,2-dichloroethane	C ₂ H ₄ Cl ₂	solvent	Merk
Chloroform	CHCl ₃	solvent	Merk
Water	H ₂ O	solvent	-
Hydrochloric acid	HCl	washing raw materials	Merk

Experiments

First 0.125 grams of 2-naphthol and 2-fold molar FeCl₃.6H₂O compound (0.47 grams) are mixed and powdered together. Then a specific volume of the solvent is added, such that it does not overflow from the reactor. In addition, a spherical ball with a diameter of 9 mm is placed inside the reactor (Figure 1). After the reaction time, the reactor is removed and purification process begins. Reacted materials are eliminated from the reactor with a small needle and washed by 10% Hydrochloric acid solution to remove the minerals. Next, the organic portion of the mineral is extracted through filter paper. The product is placed in the oven for three days at 50°C. Finally, infrared spectrometer is

TABLE 1 : Comparison of different solvents yields on oxidative coupling reaction of 2-naphthol^[18]

Solvent	Y, %
Dichloromethane	23.4
1,2-dichloroethane	20.7
Chlorobenzene	18.2
Chloroform	8.4
Benzene	6
Ethanol	≈ 0

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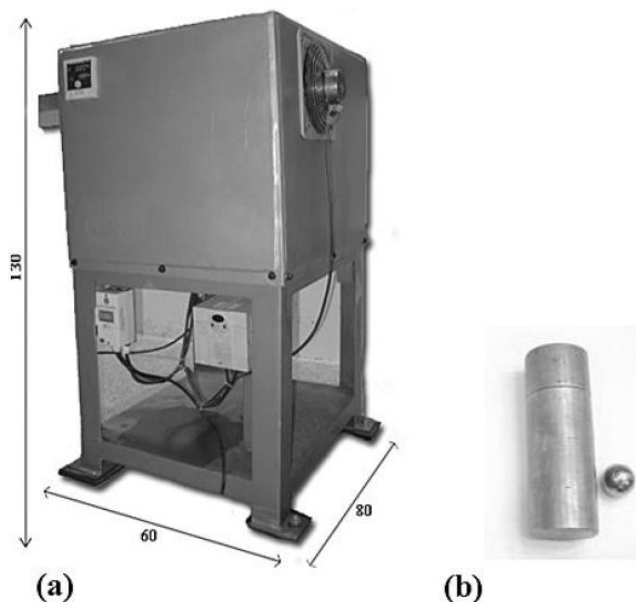


Figure 1 : (a) A ball mill; (b) a reciprocating reactor with a spherical ball

used in order to analyze and identify the functional groups and then the conversion is calculated for each reaction, individually.

There are a few analytical methods that the diagram of the spectroscopic data can be used in order to determine the concentration of the chemical groups by using the infrared spectroscopy. Significance of the qualitative methods of analysis is even much more than the quantitative analysis. According to the Beer-Lambert law, peak intensity absorbed is expressed by the Eq. (1)^[20].

$$A = a \times b \times c, \quad (1)$$

where A , a , b and c are the intensity of the peak depending on absorption that is based on the peak height, the extinction coefficient, sample thickness and concentration of the desired component, respectively^[20].

IR absorption information is considered with wave numbers on x-axis and absorption intensity or transmittance on y-axis, generally. A and T are related by a logarithmic Eq. (2)^[21].

$$A = \log_{10} (1/T) = -\log_{10} T, \quad (2)$$

where T is transmittance^[21]. According to Eq. (3), the ratio of different groups concentrations on the surface of the samples are obtained from absorption intensity peaks corresponding to the groups, because the thickness and absorption coefficients for both samples are the same

$$A_1/A_2 = c_1/c_2, \quad (3)$$

where 1 and 2 are related to two components^[20].

RESULTS AND DISCUSSION

In TABLE 3, the conversions of the reaction, which are calculated according to Eq. (3), are shown in presence of chlorobenzene, 1,2-dichloroethane, chloroform and water as solvents and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as catalyst. chlorobenzene is a non-polar compound due to the presence of chlorine in molecular structure. As can be inferred from the TABLE 3, the conversion in this case is much less than that when water is the solvent. Highest conversion is achieved when all parameters are in the maximum amounts. Due to non polarity of chlorobenzene, the lower conversion is achieved compared to above state. It is observed that chlorobenzene is insoluble in 2-naphthol during the test. The best conversion in presence of chlorobenzene is 75.5 %.

TABLE 3 : Conversion of the reaction in presence of chloroform, 1,2-dichloroethane, chlorobenzene and water as solvents: (a) chloroform; (b) 1,2-dichloroethane; (c) chlorobenzene; (d) water

Frequency, Hz	t, min	V, ml	Conv ^a , %	Conv ^b , %	Conv ^c , %	Conv ^d , %
10	10	0.1	22.1	53	27.8	58.8
10	15	0.1	24.3	61.67	31	68
10	10	0.2	25.67	68.6	33	75.3
10	15	0.2	32.33	71.2	35.5	79
15	10	0.1	33.4	73.5	36.8	78
15	15	0.1	34	76.78	40	87
15	10	0.2	39.54	80.5	58.7	91
15	15	0.2	43.1	84.2	75.5	98.3

Ethylene chloride includes two chlorine atoms and symmetry in its chemical structure. Subsequently, it would be a better option compared to chlorobenzene. The conversion is greater in comparison with when chlorobenzene is solvent, because of chlorine atoms, polarity and higher electronegativity difference of 1,2-dichloroethane.

Molar mass can also be considered as a parameter of the solvents excellence. Molar mass of 1,2-dichloroethane and chlorobenzene are 98.96 g/mol and 112.56 g/mol, respectively. Near 70 Hz, it is possible to gain high conversion in shorter time of about 5-6

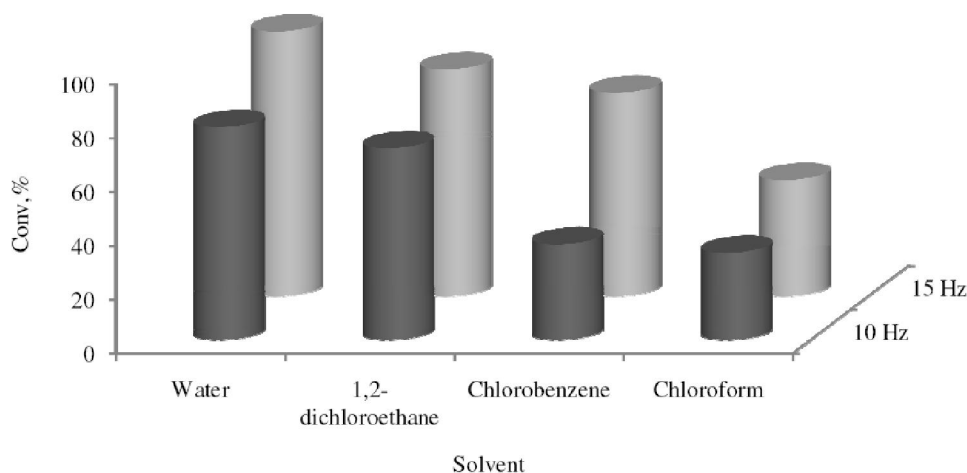


Figure 2 : Three-dimensional diagram of binaphthol conversion with four solvents, for frequencies of 10 and 15 Hz, with a reaction time of 15 minutes and solvent volume of 0.2 ml

minutes in presence of 1,2-dichloroethane. It can be distinguished from TABLE 3 that the yield would change greatly by noticeable change in frequencies. If the reactor was considered with higher volumes, the possibility of using larger volumes of solvents would have been investigated.

Crystallization of water in the structure of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ can partly provide a reaction in wet conditions. Exposure of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ to outdoor leads to this chemical reaction with the surrounding environment. Moreover, water molecules are linked to the crystallization of the salt components. In other words, a hydrated salt such as ferrous chloride crystals is a combination of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ with water.

Water is the best solvent for the oxidative coupling reaction of 2-naphthol in wet conditions because of formation of hydrogen bonds with polar structure and also its availability and non-toxicity (TABLE 3).

In Figure 2, three-dimensional diagram of binaphthol conversion with four solvents, for frequencies of 10 and 15 Hz, with a reaction time of 15 minutes and solvent volume of 0.2 ml is presented. According to Figure 2, it could be compared the performance of solvents, more efficiently. As can be seen, there will be a little difference in the conversion of binaphthol by using chloroform and chlorobenzene for low frequencies.

Oxidative coupling of 2-naphthol has also been carried out in dry state without solvent by Shayesteh. It was achieved the conversion of 95 % with frequency of 30 Hz in 12 minutes. Lack of conversion is one of the problems of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in less than 20 Hz frequency (TABLE 4)^[22].

TABLE 4 : Effect of frequency on the conversion of the reaction without solvent^[22]

Frequency, Hz	10	20	30	50	60	70
t, min	60	30	12	8	7	7
Conv, %	≤ 10	≥ 99.5	≥ 99.5	≥ 99.5	≥ 99.5	≥ 99.5

It is also observed that 9 mm ball is trapped in sticky dough even after an hour. Consequently, the ball did not move and the energy of the ball is not given to raw materials. As a result, the measured conversion is minor. Increased frequency is equivalent with increasing the number of reciprocating reactors in a second. Thus, the number of death points increases per unit time. This issue makes ball harder to hit reactor sections and more energy import to raw materials. The number of their strokes and speeds become higher with increasing frequency. As a consequence, it is expected that the conversion of chemical reaction increases with growth in frequency^[22].

According to Figure 3, there is a rapid progress at the beginning of the reaction and at high frequency. As an example, the conversion of 2-naphthol is 32.8% after two minutes at a frequency of 30 Hz, while the conversion is 72.7% at a frequency of 50 Hz^[22].

Non-polar solubility of a solid in a non-polar liquid depends on two factors: melting point and melting enthalpy. When the solid dissolves, the liquid solution is obtained. High melting temperatures and enthalpies solids show greater solubility. This difference is due to the stronger gravitational forces on objects that their crys-

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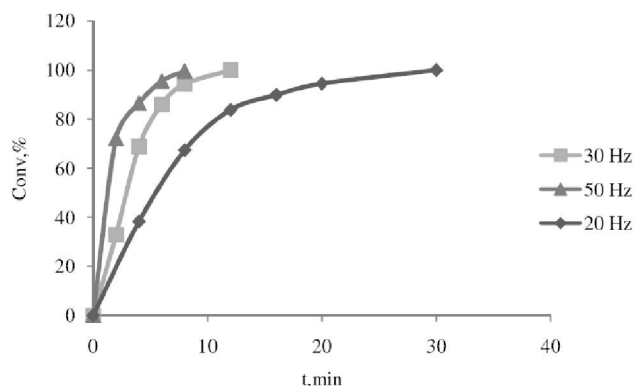


Figure 3 : Effect of reaction time on the conversion of 2-naphthol in the dry state^[22]

tals have high melting temperatures. During the solution, it should be overcome these forces. Despite having two benzene rings in its structure, 2-naphthol is considered a non-polar solid. However, it has a polar head but that is non-polar solid generally, due to the OH group. Melting point and melting enthalpy of 2-naphthol, which are both great values, are 390 K and 18.79 kJ/mol, respectively. In TABLE 5, polarity indexes, solubility in water in 20°C and boiling points for all used solvents of this reaction is shown.

TABLE 5 : Comparison of melting point, polarity index and solubility of solvents in water

Solvent	b.p, °C	Solubility in water in 20 °C, g/100 ml	Polarity index
1,2-dichloroethane	84	0.87	3.5
Chlorobenzene	131	Very low	2.7
Water	100	-	10
Chloroform	61.2	0.8	4.1

Temperature can be considered as an important factor in increasing the conversion. Rising temperatures cause faster melting of compounds and reaction progress. Due to high boiling point of hydrogen in the structure of chlorobenzene, it is possible to create conversion of binaphthol at high temperatures. Pressure can also be evaluated as a parameter in reaction enhancement. Raising Pressure leads to a decreased cross-link and increased density.

Figure 4 and TABLE 6 show binaphthol conversion with the method of this study and other methods to investigate the oxidative coupling reaction proceeded in a wet state. It is evident that water is the best solvent among the solvents mentioned. 1,2-dichloroethane and dichloromethane can also improve the conversion of binaphthol by providing appropriate reaction conditions. In TABLE 6, different times and temperature condi-

TABLE 6 : Conversion of reaction in different times and temperature conditions: (a) Joseph research^[23]; (b) present research; (c) Takizawa research^[24]

Solvent	t	Temp, °C	Conv., %
Acetonitrile ^a	24 hr	81	50
Chlorobenzene ^a	24 hr	132	70
Chlorobenzene ^b	15 min	25	75.5
1, 2-dichloroethane ^a	12 hr	83	90
1, 2-dichloroethane ^b	15 min	25	84.2
1, 2-dichloroethane ^c	24 hr	30	99
Chloroform ^c	24 hr	30	40
Chloroform ^b	15 min	25	43.1
Toluene ^a	20 hr	110	35
Water ^b	15 min	25	98.3

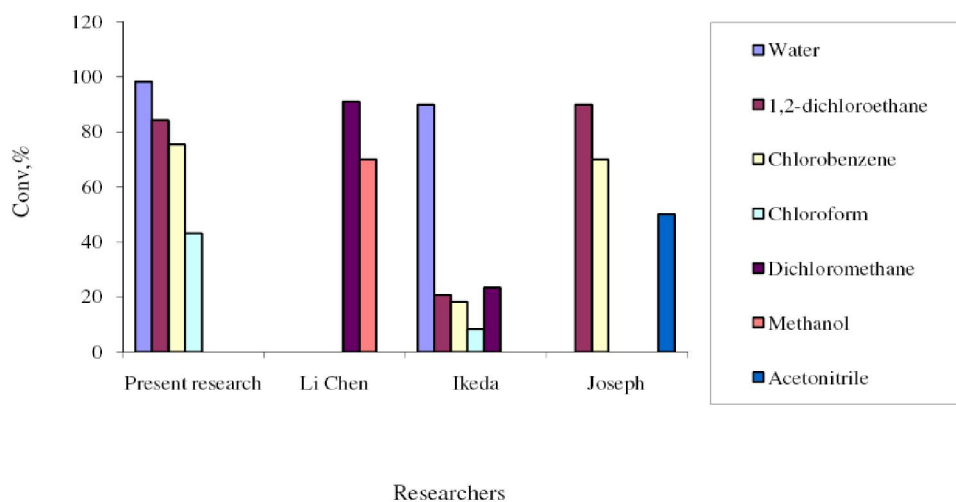


Figure 4 : Comparison of performance of our method in terms of conversion and with three other methods to produce binaphthol^[17,18,23]

tions are classified too.

To perform oxidative coupling of 2-naphthol, which leads to the production of binaphthol, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is one of the best catalysts regardless of other investigations. To accelerate this reaction, the solvent and the frequency are considered as the most important factors. The innovation of this study is the occurrence of reaction with optimal solvent in the reciprocating reactor that can provide high frequencies up to 70 Hz; furthermore, the desired product is obtained in less time.

CONCLUSIONS

In this study, oxidative coupling reaction of 2-naphthol in presence of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, with chlorobenzane, 1,2-dichloroethane, chloroform and water as solvents was done by reciprocating reactor to produce binaphthol. This study indicated that the proposed method has better conversion compared to other methods. In this research, the measured parameters are type and volume of the solvent, time of reaction and frequency. In fact these parameters are more effective than others. In the frequencies of near 70 Hz, it is possible to gain high conversion in shorter time of about 2-3 minutes. All mentioned solvents are useful solvents because of polarity and having chlorine atoms in their structures.

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