

**EPOXIDATION OF SOYBEAN OIL OVER
MESOPOROUS MoO₃/Ti-SBA-15 AND Ti-SBA-15
CATALYSTS**

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ABSTRACT

EPOXIDATION OF SOYBEAN OIL OVER MESOPOROUS MoO₃/Ti-SBA-15 AND Ti-SBA-15 CATALYSTS

In this study, it was aimed to develop heterogeneous acidic mesoporous catalysts for epoxidation of soybean oil. For this, Ti-SBA-15 catalysts were prepared by hydrothermal synthesis with two Si/Ti molar ratios (10, 20). MoO₃/Ti-SBA-15 catalysts were prepared by impregnating on the prepared Ti-SBA-15 catalysts. Two different loadings (8 and 12 %) were performed. The soybean oil epoxidation tests were performed in Radley multistation glass reactor system by hydrogen peroxide in ethyl acetate at 75 °C with stirring rate of 900 rpm. For comparison purposes, homogeneous catalysts tests were also performed with H₂SO₄.

The catalysts were found to have mesoporous structure. Titania was successfully incorporated into SBA-15. Increasing titania content did not change acidity significantly. Loading of MoO₃ decreased the surface area of Ti-SBA-15. Molybdenum loading increased the acidity of the catalysts. The acidity of MoO₃/Ti-SBA-15 with 8 % wt MoO₃ loading and 10 Si/Ti mole ratio was the highest.

The catalysts showed different activities in epoxidation of soybean oil. Some catalysts deactivated. Others showed that the soybean oil conversion and selectivity to epoxides increased with the acidity of the catalysts. The most active and selective catalyst was found to be 8% MoO₃/Ti-SBA-15(10) which gave 35.6 % soybean oil conversion and 35.6 % selectivity to epoxides.

ÖZET

MEZOGÖZENEKLİ MoO₃/Ti-SBA-15 VE Ti-SBA-15 KATALİZÖRLERLE SOYA YAĞI EPOKSİDASYONU

Bu çalışmada, soya yağının epoksidasyonu için asidik mezogözenekli heterojen katalizörler geliştirilmesi amaçlanmıştır. Bunun için, Ti-SBA-15 iki farklı Si/Ti mol oranlarında hidrotermal sentez ile hazırlanmıştır. MoO₃/Ti-SBA-15 katalizörü, hazırlanan Ti-SBA-15 katalizörlerine molibdenumun emdirme yöntemiyle yüklenmesi ile hazırlanmıştır. İki farklı yükleme miktarı (8 % ve 12 %) yapılmıştır. Epoksidasyon reaksiyonu testleri etil asetat içinde hidrojen peroksit ile 900 rpm karıştırma hızıyla Radley cam reaktör sisteminde gerçekleştirilmiştir. Karşılaştırma amacıyla, homojen katalizör testleri de H₂SO₄ ile gerçekleştirilmiştir.

Katalizörün mezogözenekli bir yapıya sahip olduğu bulunmuştur. Titania, SBA-15'e başarılı bir şekilde eklenmiştir. Artan titanya miktarı asitliği önemli ölçüde değiştirmemiştir. MoO₃'ün yüklenmesi Ti-SBA-15'in yüzey alanını azaltmıştır. Ti-SBA-15 katalizörlerinin yüzey alanları MoO₃/Ti-SBA-15 katalizörlerinden önemli ölçüde daha yüksektir. Molibdenum yüklemesi, katalizörlerin asitliğini arttırmıştır. MoO₃/Ti-SBA-15'in asitliği 8 wt% MoO₃ ve 10 Si / Ti oranı ile en yüksek olmuştur.

Katalizörler, soya yağının epoksidasyonu için farklı aktiviteler göstermiştir. Bazı katalizörler aktifliklerini (deaktive) tepkime de kaybettiler. Diğerleri soya yağı dönüşümünün ve epoksitlere olan seçiciliğin, katalizörün asitliği ile arttığını göstermiştir. En aktif ve seçici katalizör 35.6 % soya yağı dönüşümü ve 35.6 % epoksit seçiciliği veren 8% MoO₃/Ti-SBA-15(10) olarak bulunmuştur.

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CHAPTER 1

INTRODUCTION

Increasing the responsibility about environmental issues and limiting supply of petroleum and fossil fuel, causes to rise the importance of renewable and environmentally friendly resources. Vegetable oils are alternative bio-source instead of limited sources. Vegetable oils are triglyceride molecules and contain unsaturated fatty acids which can be converted to valuable chemicals. They have many features which could be used in production of valuable chemicals such as polyurethane, epoxidized vegetable oil, PVC.

Soybean oil and epoxidized soybean oil has unlimited and promising aspects. They play important role in comparison with other vegetable oils and their derivatives because of great amounts of worldwide production at a low price, namely, industrially availability in large volume. There are many reasons of usage as a raw material for many application areas. Epoxidized soybean oils have stability against heat and sunlight, resistance to acid. They protect the products against to external impacts. Addition to these, they have non-toxicity, brightening, lubricating and pigment dispersivity properties. In consequence of these excellent properties, epoxidized soybean oil has various application areas. Epoxidized soybean oil is used as a raw materials for polyurathane foams, detergents, lubricants, surface paints and adhesives, pigment dispersing agent. Besides, it is used in different kind of application areas that include flavor, coatings, agricultural and pharmaceutical materials.

Epoxidized soybean oil is produced by epoxidation reaction of double bonds in soybean oil. It is produced by mostly using peracid process. In the presence of mineral acid, synthesis of peracid is formed and used in epoxidation reaction. Furthermore, epoxidation reaction is carried out by using heterogeneous catalysts, enzyme or ion exchange resins in the presence of an oxidant (hydrogen peroxide) in an appropriate solvent (ethyl acetate, tert-butanol). Selection of solvent and oxidant is an important role in terms of performance on epoxidation reaction (Saurabh et al. 2011).

There are different types of catalysts for epoxidation of vegetable oils. These catalysts can be divided as homogeneous and heterogeneous. Examples of catalyst that

used in epoxidation of vegetable oils or fatty acids, are mineral acids (HCl, H₂SO₄, HNO₃), amorphous Ti/SiO₂, Ti-MCM-41, ion exchange resin, transition metal complexes, alumina, enzymes. Acid catalysts are used as a catalyst industrially and provide fast process for epoxidation reaction. However, they cause some drawbacks such as difficult separation, corrosion problems, toxic waste. This lead to search and use new catalyst like as heterogeneous catalysts that overcome these drawbacks. Heterogenous catalysts can be developed with regards to needs of epoxidation reaction. Their textural properties such as surface area, pore size, acidity can be improved, therefore this ensures better results on performance of epoxidation reaction (Abdullah et al. 2010).

Solvents and their features play important role in epoxidation reaction like as many other reactions. Solvents that are used in epoxidation of vegetable oils or their derivatives, are ethyl acetate, toluene, n-hexane, tert-butanol, acetonitrile. They are classified by two groups such as polar and non-polar solvents. Polarity is related to dielectric constant of solvent. When evaluated the polarity of solvents that are used in epoxidation reaction, toluene and n-hexane are non-polar solvents. Besides, ethyl acetate and acetonitrile are polar aprotic solvents whereas tert-butanol is polar protic solvent. Briefly, protic solvent have O-H or N-H bonds and these bonds may act as a proton donor. Aprotic solvent lack O-H or N-H bonds. In the light of results about selection of solvents, polar aprotic solvents are good choice for epoxidation of soybean oil (Rios et al. 2005).

According to literature about epoxidation of vegetable oils, it was indicated that affecting reaction factors were temperature, reaction time, oxidant to double bond molar ratio, solvent type, oxidant type. Additionally, catalyst properties (acidity, acid site character) are as important as other factors as mentioned previously.

In this study, mesoporous heterogeneous catalysts, as Ti-SBA-15 with different Si/Ti mole ratio (10, 20) and loaded with MoO₃ were synthesized and tested for epoxidation of soybean oil. Ti-SBA-15 catalysts were prepared by hydrothermal synthesis method while MoO₃ was loaded on Ti-SBA-15 catalyst by wet impregnation method. Loading amounts of MoO₃ were 8 wt% and 12 wt% for this purpose. Prepared catalysts were tested in epoxidation of soybean oil.

CHAPTER 2

EPOXIDATION

2.1. Vegetable Oils

Vegetable oil is the cheapest and most abundant biological feedstock. They are alternative sources to nonbiodegradable and nonrenewable petroleum feedstocks. Furthermore their ready availability, cost effectiveness and structural and functional properties make them good and favorable choice as a renewable resource. Vegetable oils are used for wide applications ranging from lubricants, coatings, epoxy resin to polymer additives. Rubber seed oil, sunflower oil, castor oil, canola oil, mahua oil and soybean oil are some of vegetable oils and they are used for many purposes in the industry. Vegetable oils are made up predominantly of triglycerides which are esters of glycerol and three fatty acids. Fatty acids of vegetable oils change in length from 14 to 22 carbons in the chain and contain from one to three C=C double bonds. Chemical structure of triglyceride is shown in Figure 2.1.

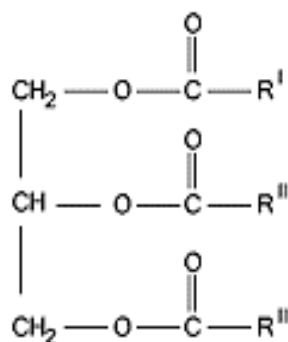


Figure 2.1. Chemical structure of triglyceride

Vegetable oils have unsaturated and saturated fatty acids. Some of them are important such as palmitic, stearic, oleic, linoleic and linolenic fatty acids. Vegetable oils are used to present epoxy groups because of having unsaturated fatty acids. Table 2.1. displays the fatty acid composition and iodine value range of different vegetable oils.

Table 2.1. Fatty acid composition and iodine value of different vegetable oils.
(Source: Danov et al. 2017)

Vegetable oil	Fatty acid composition (X:Y, where X is the number of carbon atoms and Y is the number of double bonds), wt%					Iodine value (mg/100 g)
	Palmitic (C16:0)	Stearic (C18:0)	Oleic (C18:1)	Linoleic (C18:2)	Linolenic (C18:3)	
Soybean	11.0	4.0	23.4	53.3	7.8	117-143
Palm	42.8	4.2	40.5	10.1	-	44-58
Rapeseed/Canola	4.1	1.8	60.9	21.0	8.8	110-126
Sunflower	5.2	2.7	37.2	53.8	1.0	110-143
Tallow	27.0	7.0	48.0	2.0	-	35-48
Lard	26.0	11.0	44.0	11.0	-	45-75
Butterfat	26.0	11.0	28.0	2.0	-	29-41
Groundnut	11.4	2.4	48.3	31.9	-	80-106
Cottonseed	21.6	2.6	18.6	54.4	0.7	90-119
Coconut	9.8	3.0	6.9	2.2	-	6-11
Palm kernel	8.8	2.4	13.6	1.1	-	14-24
Olive	13.7	2.5	71.1	10.0	0.6	75-94
Corn	10.9	2.0	25.4	59.6	1.2	102-130
Linseed	5.5	3.5	19.1	15.3	56.6	168-204
Sesame	9.0	6.0	41.0	43.0	1.0	103-116
Castor	1.5	0.5	5.0	4.0	0.5	82-88

Soybean oil (SBO) is one of the most available vegetable oil, has lower cost in the world. It provides easy conversion to fine chemicals when compared to other vegetable oils. Important reasons of preferring soybean oil as a desirable biomass in many reactions, are that it is renewable, sustainable, cost effective and has lubricating property. Soybean oil has different fatty acids that are divided from two groups. They are unsaturated and saturated fatty acids. These fatty acids of soybean oil are demonstrated in Table 2.2.

Table 2.2. Soybean oil composition.
(Source: Saremi et al. 2012)

Soy Fatty Acid	Structure			%
Unsaturated	Palmitic	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	C 16: 0	11
	Stearic	$\text{CH}_3(\text{CH}_2)_{16}\text{COOCH}_3$	C 18: 0	4
Saturated	Oleic	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOCH}_3$	C 18: 1	26
	Linoleic	$\text{CH}_3(\text{CH}_2\text{CH}=\text{CH})_2(\text{CH}_2)_7\text{COOCH}_3$	C 18: 2	52
	Linolenic	$\text{CH}_3(\text{CH}_2\text{CH}=\text{CH})_3(\text{CH}_2)_7\text{COOCH}_3$	C 18: 3	7

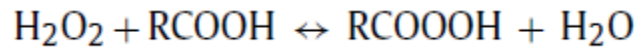
Epoxidized vegetable oils are very attractive raw material for a wide range of versatile application areas. Because, oxirane ring in the epoxide structure is very reactive part in order to prefer as a raw material. This property makes it a suitable candidate for conversion of fine chemicals in the industry.

2.2. Epoxidation of Vegetable Oils

Epoxidation of vegetable oil is a reaction which C=C double bonds in vegetable oil convert to oxirane ring (epoxide) in the presence of catalyst and oxidant in a suitable solvent. Epoxidation is one of the most important double bond addition reactions. Epoxide specifies three-membered cyclic ether where an oxygen atom is joined to each of two carbon atoms. There are several epoxidation methods in the literature. One of them is peracid process, namely it is called conventional method. Furthermore, epoxidation with acid ion exchange resin, epoxidation using enzymes are other methods. Addition to these, epoxidation using metal oxides is a promising and developing method at the present time (Saurabh et al. 2011).

Epoxidation reaction is large topic in terms of nature of sources, usage of catalysts and reaction conditions. If source materials as a reactant of reaction are investigated, epoxidation can be divided by several groups such as epoxidation of vegetable oils (cottonseed oil, mahua oil, soybean oil etc.), epoxidation of alkene (limonene, cyclooctane etc) or epoxidation of FAME (fatty acid methyl ester such as methyl oleate) (Abdullah et al. 2010).

Peracid process of epoxidation of vegetable oil is mostly available in the industry. This process include epoxidation with peroxyacetic acid and peroxyformic acid in the presence of mineral acids like sulphuric, acetic or formic acid or strongly acidic ion exchange are used as catalyst. Mineral acids such as H_2SO_4 , HNO_3 , HCl , H_3PO_4 are used in the formation of peracids. Formation of peracids are carried out in situ method or synthesis in different reactors. The in situ method is used mostly common for synthesis of peracids in large scale operation. The peracids are produced by reaction of hydrogen peroxide with acetic acid or formic acid. Consequently, peroxyacetic acid acts as an oxidizing agent in the epoxidation reaction. The performic acid formation in the aqueous phase is indicated in the following reaction:



2.1

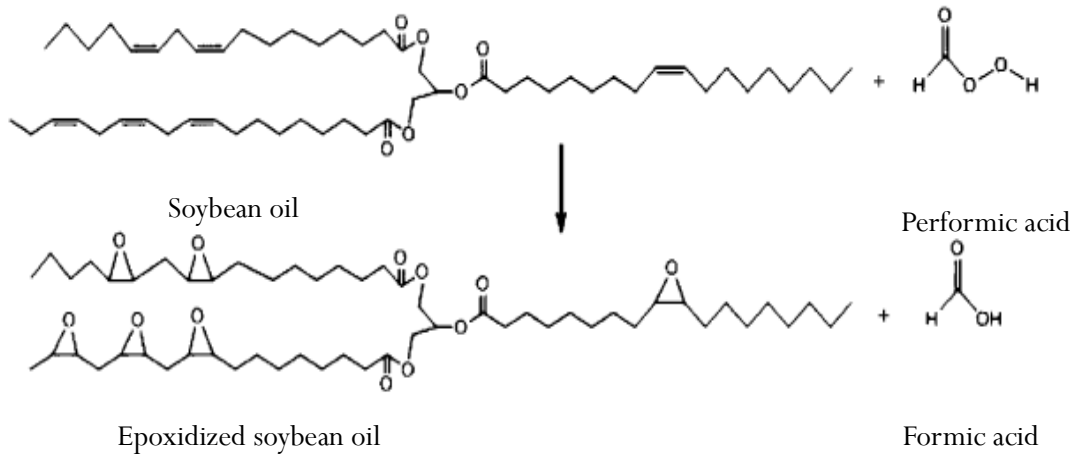


Figure 2.2. Reaction mechanism of epoxidation via peracid process
(Source: Santacesaria et al. 2011)

According to scheme above, peracid process has mainly two reactions. First reaction refers to formation of peracid (performic acid) by reaction of formic acid in the presence of hydrogen peroxide. Then, second reaction indicates consumption of peracid with ethylenic unsaturation of oil (soybean oil) in epoxidation.

There are many products which can be obtained from epoxidation of vegetable oils. The possible products of epoxidation of soybean oil with CH_3ReO_3 catalyst in the presence of hydrogen peroxide, are shown in Figure 2.3. They are monoepoxides, diepoxides, triepoxides and their diols. (Sales et al. 2002)

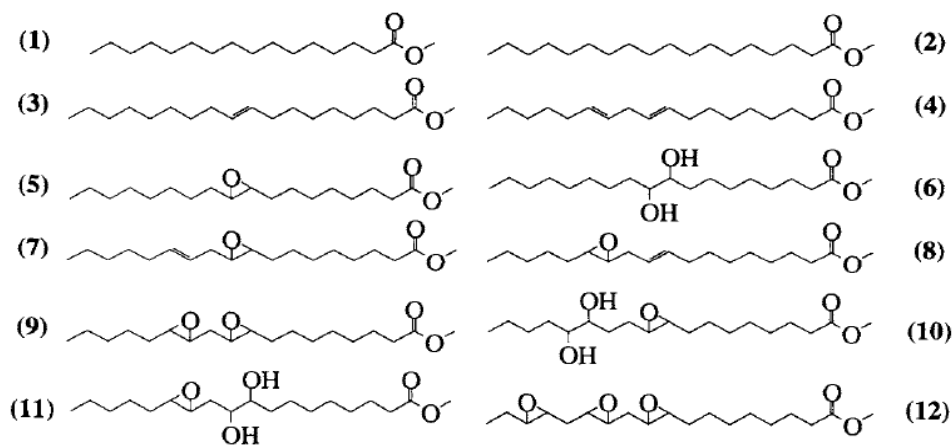


Figure 2.3. The products obtained from epoxidation of soybean oil using $\text{CH}_3\text{ReO}_3/\text{H}_2\text{O}_2$.

(Source: Sales et al. 2002)

If the reaction kinetics is considered, first reaction is slower than second reaction. Moreover, the rate of peracid formation increases with mineral acids especially sulfuric acid. However, strongly acidic catalyst tend to speed up side reactions such as ring opening reaction (oxirane cleavage). Example of side reaction during epoxidation reaction is displayed in Figure 2.3 (Sienkiewicz et al. 2016). In the presence of strong acid catalyts, it leads to form many side products such as diols, hydroxyesters, dimers. (Campanella et al. 2005).

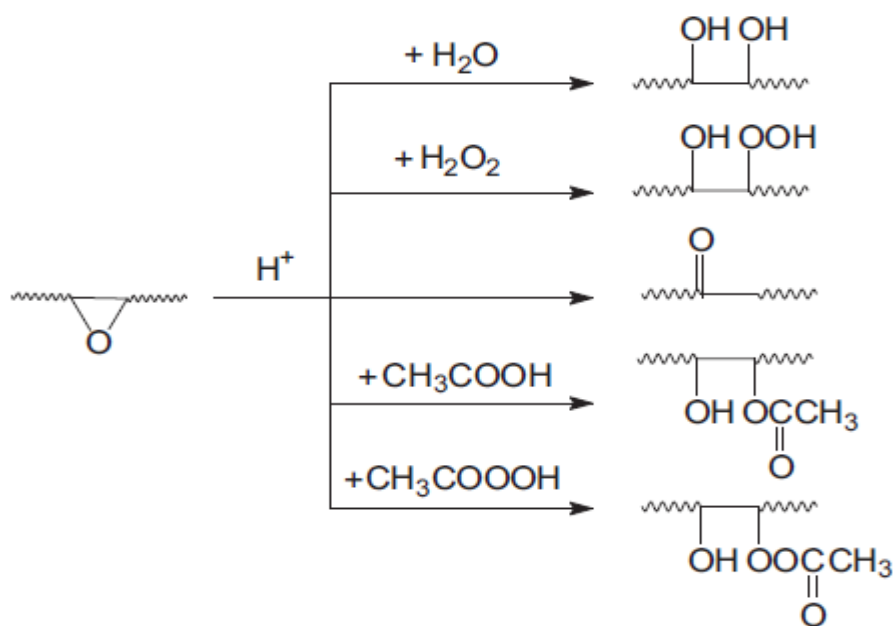


Figure 2.4. Side reaction during epoxidation reaction in peracid process (Source: Sienkiewicz et al. 2016)

Although this conventional process provides efficient, low cost, easily available operation, it has many drawbacks in terms of safety and operational problems. Separation is difficult since catalyst and reaction mixture are in the same phase. Besides, removal of acidic byproducts is not easy. Because of the usage of inorganic acids, there are corrosion problems for experimental equipments. For handling, this process causes huge amount of acidic waste materials. Furthermore, handling is more complicated than heterogeneous catalytic system. Also, side reactions such as hydrolysis of the ester groups, oxirane ring opening reaction may occur during the epoxidation reaction. As a consequence of these disadvantages of homogeneous catalytic system that includes the peracid process, new alternative catalytic systems are needed in order to overcome these drawbacks previously. This alternative refers to heterogeneous catalytic epoxidation of vegetable oils.

CHAPTER 3

LITERATURE SURVEY

In this chapter, different investigations performed over epoxidation reaction are reviewed. This part is divided into two main topics as homogeneously catalyzed epoxidation reactions and heterogeneously catalyzed epoxidation reactions.

3.1. Epoxidation By Homogeneous Catalysts

Sales et al. (2000) investigated that epoxidation of soybean oil catalysed by CH_3ReO_3 catalyst with hydrogen peroxide as an oxidant. The effect of nitrogen containing bases on the reaction in terms of activity and selectivity of the catalyst was observed. Epoxidation was performed in the presence of pyridine and other bases (4-,3-,2-picoline, pyrazol etc.) and results were evaluated based on these two topics. Epoxidation reaction mechanism is given in Figure 3.1. In this mechanism, A reacts with two hydrogen peroxide molecules to form C. Reaction rate of A is much higher at the room temperature. C is the intermediate material for the epoxidation of alkenes. In the reaction, it delivers one oxygen atom to alkene, forms to epoxide product and then regenerates to B.

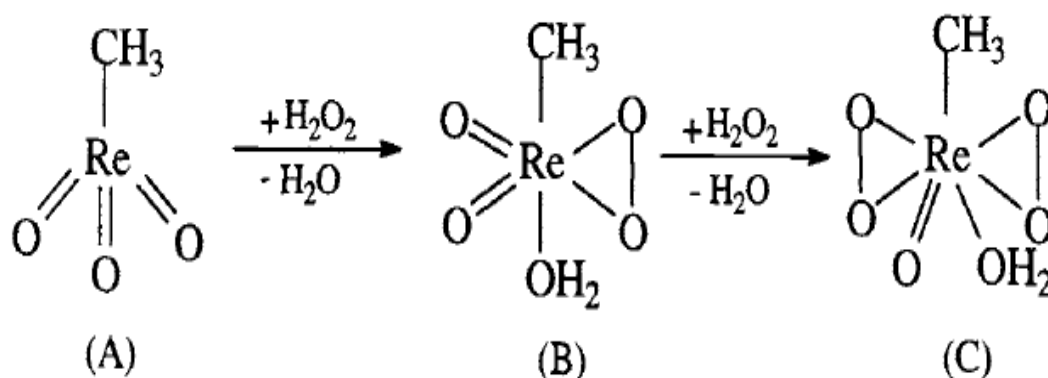


Figure 3.1. Formation of peroxo and bis-peroxo species from CH_3ReO and H_2O_2
(Source: Sales et al. 2000)

Products of epoxidation reaction reacted with methanol to produce their methyl ester forms. Therefore, the methyl esters were analysed by gas chromatography and their structures were examined by GC/mass spectrometry. Additionally, H-NMR, C-NMR and IR analyses were carried out for product analysis. It could be said that CH_3ReO_3 was active and promising homogeneous catalyst for epoxidation of soybean oil. Furthermore, the yield of this process might be enhanced by increasing amount of nitrogen containing bases.

Goud et al. (2006) focused on epoxidation of mahua oil by hydrogen peroxide in the presence of two inorganic acids (H_2SO_4 and HNO_3). At the same time, many reaction parameters such as stirring speed, temperature, $\text{H}_2\text{O}_2:\text{C}=\text{C}$ molar ratio, oxygen carrier, $\text{CH}_3\text{COOH}:\text{C}=\text{C}$ molar ratio, H_2SO_4 concentration were examined with regard to their effects on the reaction. In brief of outcomes, stirring speed did not have influence on the reaction. All tests were carried out at 2500 rev/min. To evaluate the effect of $\text{H}_2\text{O}_2:\text{C}=\text{C}$ on conversion to oxirane, range of 0.8 to 2.0 was performed and it was found that optimum result of conversion was obtained with 1.1 as $\text{H}_2\text{O}_2:\text{C}=\text{C}$ molar ratio. When evaluated acetic acid to double bond molar ratio, 0.5 mole/mole value achieved optimum result with regard to relative conversion to oxirane. If two inorganic acids were compared, sulphuric acid was accepted as more suitable catalyst for epoxidation. Addition to comparison of acids, acid concentration was looked through and best relative conversion to oxirane was obtained at 2.0 % of H_2SO_4 . As a result of temperature impact on the epoxidation reaction, increase in temperature demonstrated a substantial effect in the peracid process. It was indicated that higher temperature reached to higher conversion to oxirane for 4 h of reaction time. But with increasing reaction time, conversions to oxirane were not stable and declined visibly.

For making proper observations, oxirane oxygen was determined by analytical method which means to titration technique by using hydrobromic acid solution in acetic acid. Besides, iodine value was determined by Wij's method. With the determined oxirane content values, the relative fractional conversion to oxirane was computed by the following equation;

$$\text{Relative conversion to oxirane}(RCO) = \frac{OO_e}{OO_t} \quad (3.1)$$

While OO_e is the experimental oxirane oxygen content, OO_t is theoretical maximum oxirane oxygen which was calculated as 5.25 % by the another equation;

$$OO_t = \frac{\left(\frac{IV_o}{Ai}\right)}{100 + \left(\frac{IV_o}{2Ai}\right) * Ao} * Ao * 100 \quad (3.2)$$

Ai and Ao are the atomic weights of iodine and oxygen as 126.9, 16.0 readily. IV_o is the initial iodine value of oil.

A similar work was carried by Dinda et al. (2008) for the epoxidation of cottonseed oil by aqueous hydrogen peroxide catalysed by inorganic acids. In this study, peracid process was performed by hydrogen peroxide with glacial acetic acid in the presence of H_2SO_4 and $HCOOH$, HNO_3 , H_3PO_4 and HCl . Catalytic activities of these different acids were observed and compared in epoxidation reaction. Several affecting factors were examined as in investigations of Goud et al. (2006). Oxirane oxygen content was not influenced by changing stirring speed between 600 and 2400 rpm. All experiments were performed at 2400 rev/min. Different temperatures were studied as $30^\circ C$, $45^\circ C$, $60^\circ C$, $75^\circ C$. The highest relative conversion to oxirane was obtained at $60^\circ C$ for 4 h of reaction time, but after 4 h conversion decreased, significantly. The highest relative conversion of iodine value was acquired at $75^\circ C$. At lower temperature, conversions of iodine value were lower but had increasing behaviour. Four $H_2O_2:C=C$ molar ratios were examined and the best result was found for $H_2O_2:C=C$ as 2.0. In comparison to CH_3COOH and $HCOOH$ as an oxygen carrier, higher conversion to oxirane was obtained from usage of $HCOOH$. In the presence of $HCOOH$, in spite of relative conversion of iodine value increased readily, relative conversion to oxirane increased and then dropped. This was attributed to side products and therefore it was not suitable oxygen carrier for epoxidation reaction.

Addition to these observations, they viewed applicability of inorganic acids as a catalyst. H_2SO_4 and H_3PO_4 had higher oxirane conversion when compared with HCl and HNO_3 . The highest conversion to oxirane was found as 70.4 % in the presence of H_2SO_4 . Lastly, H_2SO_4 amount in the range of 1% to 3% were applied. It was found that conversion to oxirane increased with increasing acid concentration up to 2% H_2SO_4 . Figure 3.2 demonstrates the effect of temperature on relative percentage conversion to

oxirane and glycol. Higher temperature decreased the reaction time needed to reach to maximum conversion to oxirane. Furthermore, higher temperature increased oxirane ring cleavage to glycol for shorter reaction time.

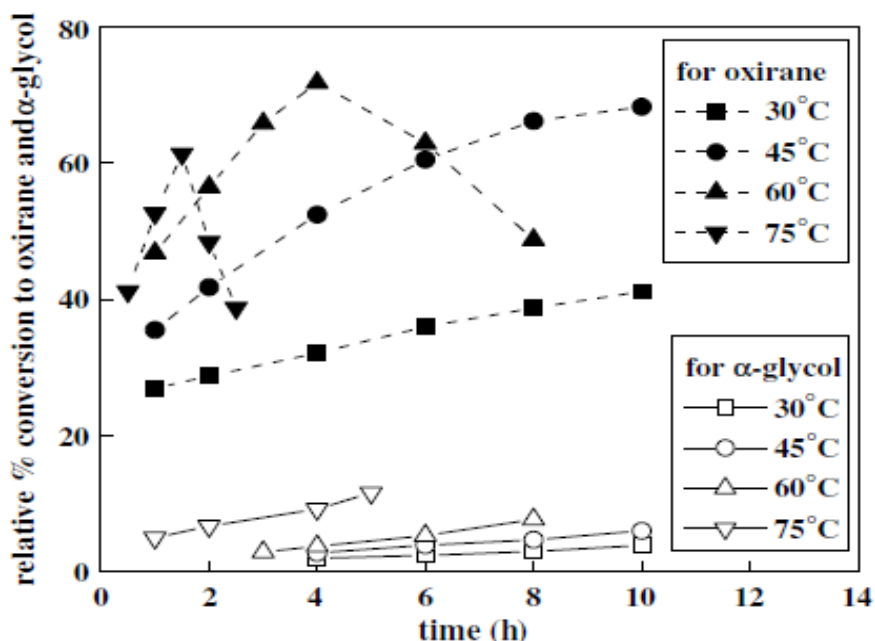


Figure 3.2. Effect of temperature on relative percentage conversion to oxirane and α -glycol. Conditions: mole H_2O_2 per mole unsaturation = 1.5; mole CH_3COOH per mole unsaturation = 0.5; H_2SO_4 = 2%; and stirring speed = 2400 ± 25 rev/min.

(Source: Dinda et al. 2008)

Farias et al. (2010) investigated that epoxidation of soybean oil with homogeneous catalyst based on a molybdenum (VI) complex in the presence of tert-butyl hydrogen peroxide as an oxygen donor in toluene. Reaction mechanism of epoxidation of an olefin with hydroperoxide in the presence of a transition metal complex was demonstrated below in Figure 3.3.

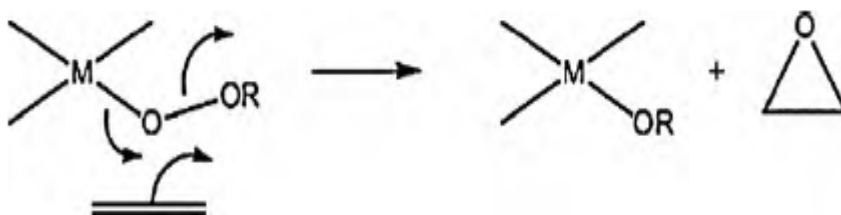


Figure 3.3. Mechanism of epoxidation of an olefin by reaction with hydroperoxide in the presence of a transition metal catalyst.

(Source: Farias et al. 2010)

Epoxidation reaction was tested for two temperatures, 80 °C and 110 °C, for 2 h reaction time. Products were examined by quantitative NMR analysis. With this analysis, catalytic activities were determined in terms of conversion, epoxidation and selectivity. Best results were obtained at 110 °C for 2 h when compared to other reaction conditions for this study. Soybean oil conversion, epoxidation and selectivity to epoxide were found as %70.1, %54.1, %77.2, respectively. This observations indicated that molybdenum (VI) complex with tert-butyl hydrogen peroxide was promising potential catalytic system for epoxidation of soybean oil.

Saremi et al. (2012) studied soybean oil epoxidation with hydrogen peroxide in the presence of formic acid as a mineral acid. In this study, peracid process was carried out to obtain epoxidized soybean oil. Product analysis were carried out by both analytical and spectroscopic methods. Titration of oxirane oxygen content as an analytical procedure was performed to determine amount of oxirane ring in epoxidized soybean oil chain. Moreover, FTIR analysis was applied to indicate functional groups of epoxidized soybean oil in the spectrum. According to results, the highest epoxy content was obtained as 6.1 %. In the light of this result, it was considered that there might some side reaction occurred. This was supported by FTIR spectrum of epoxidized oil, which showed the side reaction such as ring opening reaction.

Sienkiewicz et al. (2016) studied that epoxidation of soybean oil with different catalysts such as H₂SO₄, ion exchange resin (Amberlyst 15) and Zerolit 325, Zeolite Y, immobilized enzyme lipase B, Novozym 435. They investigated the effect of these different catalysts on the selectivity and efficiency of epoxidation reaction. Moreover, another aim of this study was to observe the catalysts reactivities in fusion process with bisphenol A. Therefore, products and different processes were compared in terms of catalytic activity and product properties. H₂SO₄ was used for comparison with other catalysts since it is most widely used catalyst in the industry. At the end of all observations, zeolite Y was not good catalyst for epoxidation of soybean oil. When compared with other catalysts in terms of soybean oil conversion and selectivity to epoxide results, Novozym 435 and H₂SO₄ had the highest conversions like as 99.7% and 73.1% respectively. Selectivity to epoxide was 100%. Although Zerolit 325 obtained moderate soybean oil conversion (62.5%), it showed the second highest selectivity to epoxide (95%) after H₂SO₄. Ion exchange resins had less catalytic activities in epoxidation of soybean oil and they had the smallest conversion and selectivity values as 44% and 10 %, separately.

Figure 3.4 shows FTIR spectra of soybean oil and products with different catalysts. Adsorption bands at 3009 cm^{-1} and 1656 cm^{-1} characterized to double bond with little intensity for soybean oil. Another adsorption band at 824 cm^{-1} presented to epoxy group for the products from different catalysts.

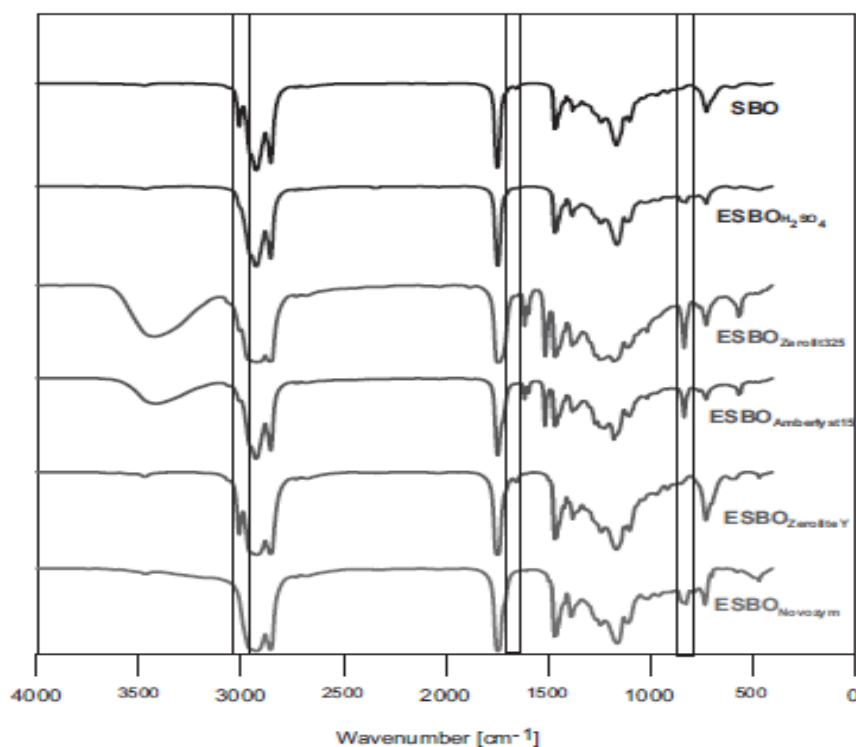


Figure 3.4. FT-IR spectra from soybean oil and products of epoxidation reaction of soybean oil in a presence of different catalysts.
(Source: Sienkiewicz et al. 2016)

In the Figure 3.5, the looks of products were demonstrated. It can be said that all products were seemed to clear yellowish liquid.

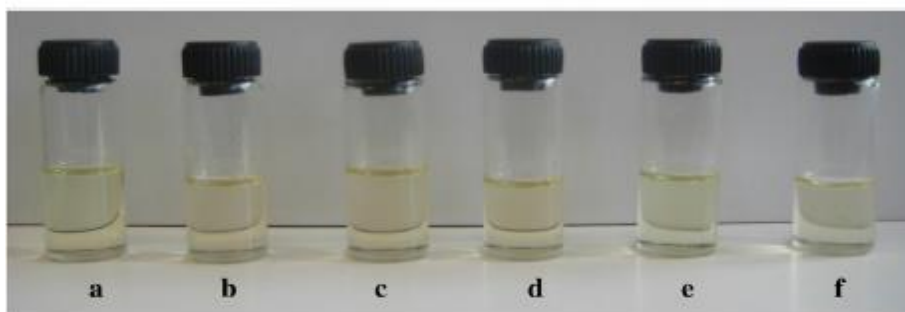


Figure 3.5. Epoxidized soybean oil: a-SBO, b-ESBO_{H₂SO₄}, c-ESBO_{Zerolit325}, d-ESBO_{Amberlyst15}, e-ESBO_{ZeoliteY}, f-ESBO_{Novozym435}
(Source: Sienkiewicz et al. 2016)

Generally, mineral acids such as sulphuric acid or formic acid are used as homogeneous catalyst in the epoxidation of vegetable oils or alkene. These acids are used industrially because of their availability. However, the presence of these mineral acids causes to many side reactions such as oxirane-ring opening to diols and other dimers formation. Furthermore, they result in corrosion problems in equipments due to the highly corrosive effect of these acids. Hence, they should be neutralized and removed from the final product. But, because of same phases with reaction mixture, separation step is too difficult. In the view of these drawbacks of mineral acids as a homogeneous catalyst, heterogeneous catalysts were needed and developed in some studies for epoxidation of vegetable oils, alkenes or FAMES.

3.2. Epoxidation By Heterogeneous Catalysts

Campanella et al. (2004) investigated the epoxidation of soybean oil and soybean methyl esters with hydrogen peroxide by an amorphous Ti/SiO₂ as a heterogeneous catalyst in tert-butyl alcohol as a solvent. Tert butanol is a polar protic solvent. In this work, the effect of some parameters such as H₂O₂:C=C molar ratio, reaction temperature was observed and assessed on epoxidation reaction. They examined three different H₂O₂:C=C molar ratio. Two of them were excess of oxidant as 5.5/1 and 1.1/1, one of them was an excess of soybean oil as 0.6/1. It was indicated that best result in conversion were achieved with the excess of oxidant molar ratios which gave almost same conversions. However, excess of soybean oil gave smaller conversion. As a result of this, optimum molar ratio was accepted as 1.1/1. Along with this examination, other parameter namely reaction temperature was evaluated. Increasing temperature affected with regard to conversion, significantly. In spite of the fact that highest conversion (almost 90%) was acquired at 90° C, it took long reaction time which was 54 h. In this study, Ti/SiO₂ was prepared by sol-gel method by using titanium isopropoxide as a precursor. Titanium was tetrahedrally present for characterization.

Rios et al. (2005) studied that epoxidation of vegetable oils by mesoporous and amorphous Ti-silicates. Ti-MCM-41 and amorphous Ti-SiO₂ catalysts were prepared with different methods and source of materials. Oleic acid methyl ester was used as reactant and tert butyl hydroperoxide was used as an oxidant in epoxidation reaction. In

catalytic test, different solvents were used in order to indicate the effect on the reaction. These solvents were toluene, acetonitrile, n-hexane and tert-butanol. Ti-MCM-41 catalysts were prepared by sol gel with four different Ti loadings (0.8, 2.2, 2.7, 2.9). These number presents the molar ratio (Ti/Si) $\times 100$. Four different Ti-amorphous silicas were used. Ti-SiO₂(2.0) was a commercial silica-titania; Ti-SiO₂(5.6) was prepared from coprecipitation of silica Aerosil; Ti-SiO₂(0.8) was prepared in the same procedure as Ti-MCM-41; Ti-SiO₂(1.6) was prepared by the same procedure as Ti-MCM-41 but without surfactant. According to XRD results, Ti-MCM-41 catalysts had hexagonal structure. It was found that Ti-SiO₂ did not have crystalline phase from XRD results. Ti-MCM-41 catalysts had larger surface area and lower pore diameter when compared to Ti-SiO₂ catalysts. FTIR spectra of Ti-MCM-41 catalysts are shown in Figure 3.6. Four significant adsorption bands were investigated. The band at 810 cm⁻¹ was related to symmetric stretching/bending of Si-O-Si. The band at 1085 cm⁻¹ with 1220 cm⁻¹ resulted from Si-O-Si asymmetric stretching. The most significant band which was at 960 cm⁻¹ referred to the incorporation of Ti into tetrahedral environment in the SiO₂ framework.

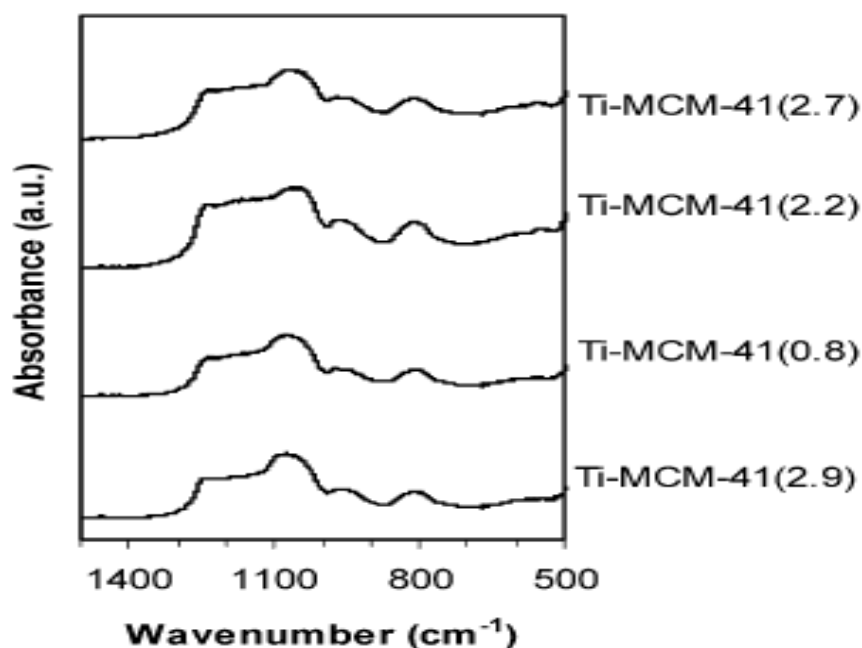


Figure 3.6. FTIR spectra for Ti-MCM-41 catalysts.
(Source: Rios et al. 2005)

After catalytic tests for Ti-MCM-41 catalysts, the effect of temperature was observed on the reaction conversion and selectivity. With increasing temperature from 25 to 100 °C, selectivity to epoxide decreased but conversion increased remarkably from 10

% to 90 %. The catalytic activities of Ti-SiO₂ catalysts in different solvents were investigated and given in Figure 3.7. In this observation, acetonitrile, tert butanol, toluene and n-hexane were used with TBHP as an oxidant while tert butanol and acetonitrile were used with H₂O₂. Best results in the sense of epoxide yield were obtained in the presence of TBHP in n-hexane as a solvent. H₂O₂ with acetonitrile and tert butanol systems had lowest epoxide yield. If the polarity of aprotic solvents were considered, order of polarity was like as; acetonitrile > toluene > n-hexane. Tert butanol is a polar protic solvent and this property influenced on activity of reaction. Polar protic solvents decreased activity of reaction.

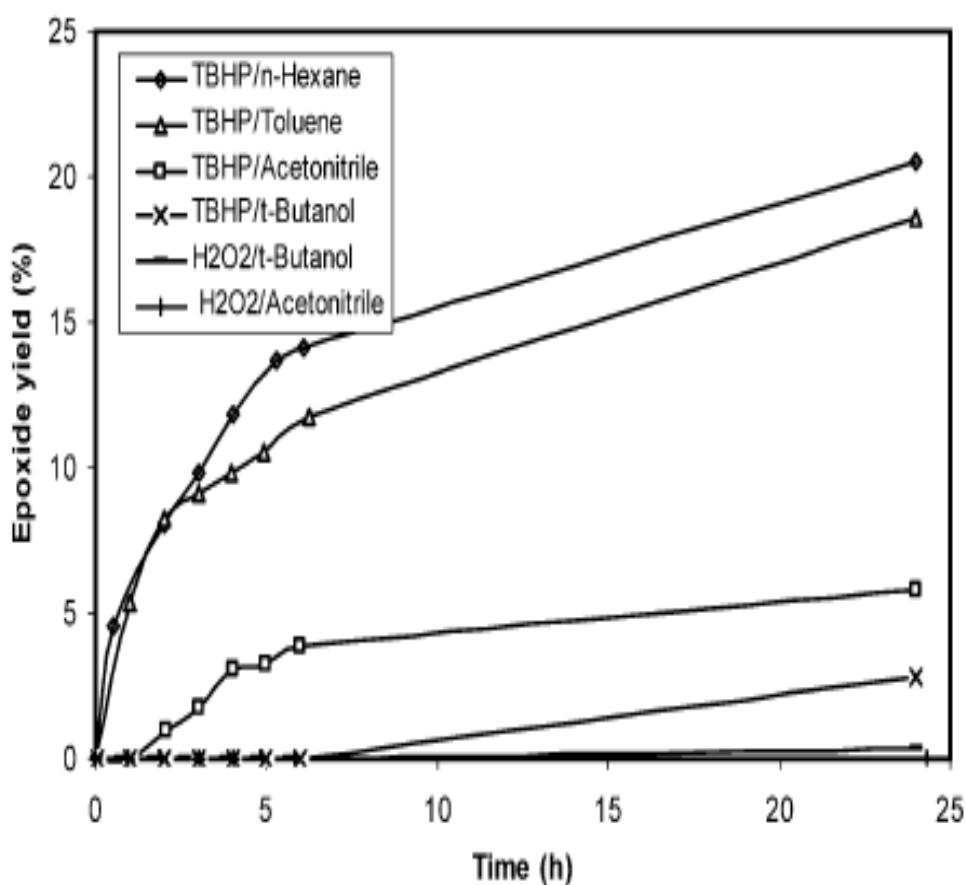


Figure 3.7. Solvent effect on the epoxidation of high oleic methyl oleate with Ti-SiO₂(1.6)D. hydroperoxide/oleate = 1.1 mol/mol, oleate/catalyst = 20 g/g, toluene/toluene = 1 g/g, temperature = 70° C.
(Source: Rios et al. 2005)

In the reusability test of Ti-SiO₂ catalysts, these catalysts had stable activities, their activity decreased barely. Consequently, after all observations, Ti-SiO₂ catalysts provided a promising system with TBHP for epoxidation of vegetable oils. In the leaching

and reusability tests of Ti-SiO₂ catalyst, there was not significant change in epoxide selectivity during four runs. The epoxide yield decreased a little bit after first run.

Guidotti et al. (2006) investigated epoxidation of unsaturated FAMES obtained from vegetable source over Ti(IV)-grafted silica catalyst. In this study, ordered and non-ordered mesoporous catalysts were compared in terms of performance on the epoxidation reaction. Typical reaction was epoxidation of mixtures of fatty acid methyl esters (FAMES) over titanium containing silica catalysts using tertbutylhydroperoxide. In this study, the FAMES mixtures contained different vegetable oils such as high-oleic sunflower oil, coriander oil, castor oil and soybean oil. The catalysts were Ti-MCM-41 (A), Ti-SiO₂ Davidson (B), Ti-SiO₂ Aerosil (C) and Ti-SiO₂ Grace (D). A, B and C were prepared from siliceous MCM-41 and SiO₂ sources with different brands by grafting titanium sites using a solution of titanocene dichloride. XRD patterns of some catalytic materials are shown in the Figure 3.8. According to the patterns, curve (a) referred to an ordered hexagonal arrangement, curve (b) and curve (c) referred to disordered arrangement. Catalysts A, B and D were porous materials while catalyst C was a non-porous material.

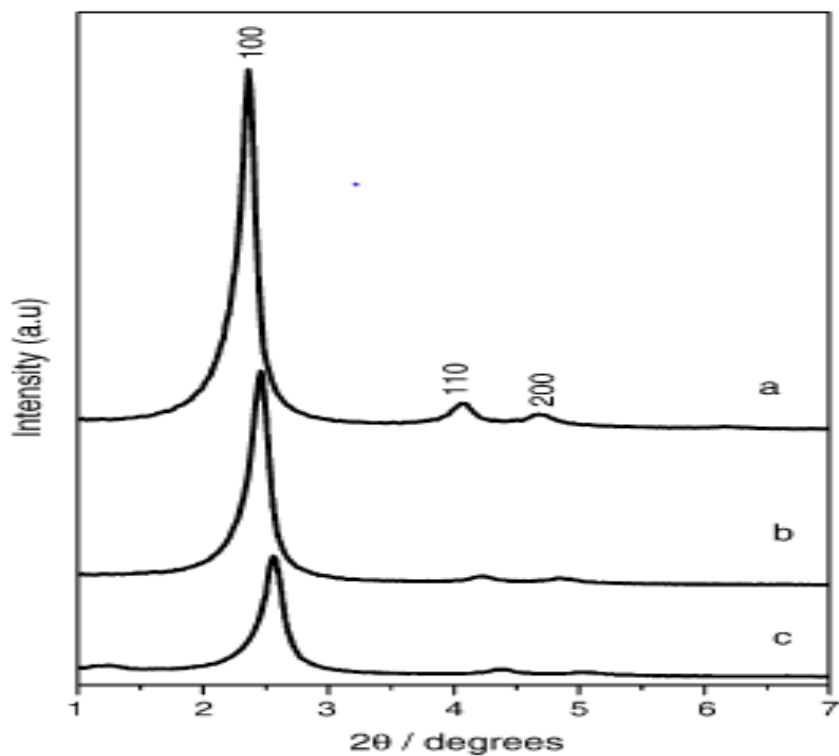


Figure 3.8. XRD patterns of (a) calcined MCM-41, (b) Ti(Cp)₂Cl₂ grafted on MCM-41 and (c) calcined Ti-MCM-41.

(Source: Guidotti et al. 2006)

Catalyst A and C gave the highest conversions (98%, 95%) for the FAMEs from high oleic sunflower oil. Catalyst B had the highest conversion (76%) as same value with both the FAMEs from high oleic sunflower oil and castor oil. Catalyst D gave the highest conversion (80%) for the FAMEs from castor oil. Selectivities of the catalysts were obtained the highest for the FAMEs from castor oil. In the recycling test, activities of catalysts A, B and C dropped by less than 10% compared to fresh catalyst, while catalyst D had activity loss of 16 %.

Studies given above shows that Ti containing catalysts, these catalysts are good candidate in terms of catalytic performance in epoxidation reaction. Titanium containing mesoporous catalysts exhibit high catalytic activity for epoxidation of olefins. Moreover, titanium loading amount and dispersion considerably influences their activity. Addition to this, their stability and catalytic activities in the reaction can be improved with proper modification and also their textural properties can be modified according to the needs of the reaction.

Serio et al. (2012) investigated the epoxidation of soybean oil catalysed by Nb₂O₅-SiO₂ in the presence of hydrogen peroxide. Nb₂O₅-SiO₂ catalyst was prepared by sol-gel method. This catalyst were prepared for three Nb₂O₅ loadings (7.12 wt.%, 13.2 wt.%, 23.0 wt.%). According to characterization of catalyst, the highest surface area and pore volume were found for the lowest Nb content (7.12 wt.% Nb). In the epoxidation test, ethyl acetate was used as a solvent. Ethyl acetate is polar aprotic solvent which was considered to promote epoxidation reaction. Epoxide products was analyzed by analytical method that was determination of iodine value and oxirane number. Double bond conversion and selectivity to epoxide values were computed with these titration methods. Nb₂O₅-SiO₂ catalyst with the smallest Nb content (7.12 wt.%) had the highest double bond conversion (30%) and the lowest selectivity to epoxide (<10%). However, for high Nb content, the lowest double bond conversion (%15) and the highest selectivity to epoxide (>40%) were obtained. Catalyst with 13.2% Nb showed moderate conversion and selectivity.

To sum up, although increase in Nb content promoted selectivity, it did not influence conversion. When considering previous conclusions, it can be said that reason of decrease in selectivity was formation of side products namely, it means side reaction which refers to ring opening reaction to form diol in the presence of water in the epoxidation reaction. Figure 3.9 presented to epoxide ring with water present in reaction environment giving place to diol.

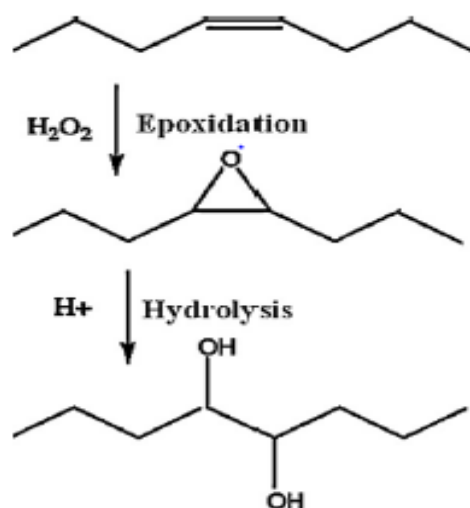


Figure 3.9. Epoxide ring with water present in the reaction environment giving place to diol.

(Source: Serio et al. 2012)

In other previous work about Nb_2O_5 - SiO_2 catalyst, it was demonstrated the lowest Nb content catalyst (7.12 wt.%) had more Bronsted acid sites on the silica surface. Increase in Nb content on the catalyst affected negatively, in other words Bronsted acid sites were reduced with this rise. Moreover, these catalysts were tested in transesterification/esterification reaction. According to outcomes of these tests, although lewis acid sites promoted epoxidation reaction, they did not support transesterification reaction. In the light of this work, Nb_2O_5 - SiO_2 catalyst can be accepted a good catalyst but it can not be preferred due to the low selectivity to epoxides.

Zhang et al (2014) studied that solvent-free epoxidation of soybean oil catalysed by peroxophosphotungstate supported on palygorskite. Palygorskite (Pal) is a hydrated magnesium aluminum silicate. It has specific textural properties in terms of moderate cationic exchange capacity, large surface area and suitable adsorption character. Pal was silylated and peroxophosphotungstate (PPT) was immobilized on it. Epoxidation was performed by using hydrogen peroxide as an oxidant without solvent. Epoxidation of soybean oil was carried out at 40 °C for three reaction time which were 60, 120, 180 min. Conversion to oxirane increased with increasing reaction time. However, epoxide yield and selectivity increased when reaction time reached to 120 min. After 120 min, epoxide yield and selectivity decreased slightly. Furthermore, effect of reaction temperature was examined by carrying out at 40, 50, 60 °C. Best results with regard to conversion to oxirane, epoxide yield and epoxide selectivity were obtained at 50 °C as 58.62 %, 18.88 % and 30.21 %, respectively. Addition to these examinations, they found that oxirane

conversion, epoxide yield and epoxide selectivity increased with increasing mass ratio between H_2O_2 and SBO from among three mass ratios (1:1, 1.25:1 and 1.5:1). Namely, 1.5:1 mass ratio gave the best results. Consequently, it was indicated that conversion to oxirane, epoxide yield and epoxide selectivity diminished mildly with increasing reaction cycle.

The literature information given above on epoxidation of epoxides provided the following information. The epoxidation of vegetable oil is carried out by different catalysts that can be divided by mainly two groups. These are homogeneous and heterogeneous catalysts. Addition to these, enzymes can be used as a new alternative system in this reaction. Examples of catalysts that used in epoxidation are acid catalysts, Ti containing silica, tungsten based catalayts, transition metal complexes, alumina, amorphous titania silica, ion exchange resin, enzymes. In the fact that, there were not many studies about epoxidation of soybean oil, especially, but mainly epoxidation of different materials such as alkene, olefin and FAME (Abdullah et al. 2010).

In the light of above information given in this chapter, it was aimed to synthesize Ti-SBA-15 catalysts with two Si/Ti molar ratio and MoO_3 loading on the Ti-SBA-15 for epoxidation of soybean oil. Additionally, H_2O_2 was used in terms of being suitable and green oxidant and ethyl acetate was taken as polar aprotic solvent in the epoxidation reaction. It was aimed to examine the influence of MoO_3 loading and Ti contents on the reaction. Furthermore, as homogeneous catalyst H_2SO_4 was tested for epoxidation of soybean oil by acetic acid and H_2O_2 for comparison.

CHAPTER 4

EXPERIMENTAL STUDY

In this study, it was aimed to prepare and test heterogeneous catalysts for epoxidation of soybean oil with hydrogen peroxide in a suitable solvent. In the direction of this aim, Ti-SBA-15 with different Si/Ti molar ratios, different amounts of MoO₃ loaded Ti-SBA-15 were prepared. Ti-SBA-15 catalyst were synthesized with Si/Ti=10 and Si/Ti=20. Prepared Ti-SBA-15 catalysts were loaded with MoO₃ for two different ratios as 8 wt% and 12 wt%. The chemicals for catalyst preparation and catalytic test are tabulated in Table 4.1.

Table 4.1. The chemicals used for catalyst preparation and catalytic test

Chemicals	Brand / Purity
Pluronic P123	Aldrich, average Mn ~ 5,800
Titanium isopropoxide (TISOP)	Sigma-Aldrich ≥ 97 %
Tetraethyl orthosilicate (TEOS)	Aldrich 98%
Ammonium heptamolydate tetrahydrate (NH ₄ 6Mo ₇ O ₂₄ .4H ₂ O)	Merck ≥99.3 %
Hydrochloric acid (HCl)	Sigma-Aldrich, 37 %
Soybean oil	Balsarı Yağ San. ve Tic. Ltd. Şti.
Acetic acid	Merck, glacial (100 %)
Hydrogen peroxide	Sigma-Aldrich 34.5-36.5 %
Ethyl acetate	Sigma-Aldrich ≥99.7 %
Sodium sulfate	Merck ≥99.8 %
Sulphuric acid	Merck, 95-97 %

Soybean oil fatty acid composition is exhibited in Table 4.2. The content of linoleic acid was the highest (51.8 %) in soybean oil. The content of oleic acid was the second highest (24.66 %).

Table 4.2. Fatty acid composition of soybean oil

Fatty acid	Structure	FA%	Limit
Miristic acid	C 14:0	0.09	max 0.2
Palmitic acid	C 16:0	11.45	8.0-13.5
Palmitoleic acid	C 16:1	0.11	max 0.2
Heptadecanoic acid	C 17:0	0.06	max 0.1
Heptadecenoic acid	C 17:1	0.06	max 0.1
Stearic acid	C 18:0	3.67	2.0-5.4
Oleic acid	C 18:1	24.66	17.0-30.0
Linoleic acid	C 18:2	51.87	48.0-59.0
Linolenic acid	C 18:3	6.71	4.5-11.0
Aracidic acid	C 20:0	0.42	0.1-0.6
Gadoleic acid	C 20:1	0.13	max 0.5
Behenic acid	C 22:0	0.45	max 0.7
Lignoseriic acid	C 24:0	0.32	max 0.5

The iodine value, oleic acid composition, refraction and colour are indicated in table. The iodine value of soybean oil was given as Table 4.3. This value is significant property because of determining unsaturation level of soybean oil. Iodine value of soybean oil was determined by Wijs method in the laboratory. This value was found as 135.6, it is close to value given for the oil.

Table 4.3. Some properties of soybean oil

Property	Value	Range
FFA % Based on oleic acid	0.15	max 0.3
Refraction	14755	14700-14760
Iodine value	136.1	125-143
colour	2	max 3

4.1. Catalyst Preparation

4.1.1. Preparation of Ti-SBA-15

Mixture of 9 g Pluoronic P-123 and 220 ml water was stirred for 2 h at 40 °C. After stirring for 2 h, a clear solution was obtained and 3.78 ml of HCl (1 M) was added to this solution and continued to stirring for 2 h. Thereafter, mixture of 2.9 ml TISOP and 21.4 ml TEOS was added. The mixture was stirred for 24 h at 40 °C. The resulting gel was transferred to the autoclave and kept at 100 °C for 24 h for hydrothermal synthesis. Final product was washed with deionized water, centrifuged, dried at 100 °C for 24 h and calcined at 550 °C for 6 h. (Sharma et al. 2012). This catalyst was referred to as Ti-SBA-15(10). Following the same procedure, another catalyst using only different amount of TISOP (1.45 ml) for Si/Ti ratio of 20, was prepared (Ti-SBA-15(20)).



Figure 4.1. Ti-SBA-15 catalysts obtained hydrothermal synthesis in the autoclave.

4.1.2. Preparation of MoO₃/Ti-SBA-15

The prepared Ti-SBA-15(10) and Ti-SBA-15(20) were loaded with 8% and 12% wt. MoO₃ as follows. A mixture of ammonium heptamolybdate tetrahydrate (NH₄6Mo₇O₂₄.4H₂O) and 250 ml of distilled water was stirred until complete dissolution and heated to 50 °C. MoO₃ loadings were 8 wt% which referred to 0,09811 g of ammonium heptamolybdate tetrahydrate used in impregnation and 12 wt% which means to 0,1471 g of precursor in same way. Then, 1 g Ti-SBA-15 was added to this solution and few drops of NH₄OH was added until pH of solution reach to 8. After that, solution was stirred for 1 h at 50 °C. Then, it was poured into the glass beaker and water was removed. After drying at 100 °C for 12 h, it was calcined at 550 °C for 3 h. The catalyst prepared with 8% loading using Ti-SBA-15(10) was named as 8%MoO₃/ Ti-SBA-15(10). The other prepared catalyst with 12% loading using Ti-SBA-15(10) was named as 12%MoO₃/ Ti-SBA-15(10). The other catalysts were prepared using Ti-SBA-15(20) were 8 % MoO₃/Ti-SBA-15(20) and 12 % MoO₃/ Ti-SBA-15(20), respectively.

4.2. Characterization of Catalysts

4.2.1. N₂ Adsorption/Desorption (BET)

Nitrogen physisorption studies were performed using Micromeritics ASAP 2010 model static volumetric adsorption instrument. The catalysts were degassed at 200 °C for 2 hours. N₂ adsorption was performed at 77 K.

4.2.2. X-Ray Diffraction (XRD)

The crystalline structures of the catalysts were determined by Philips X'Pert diffractometer with CuK α radiation. The scattering angle 2θ was varied from 5 ° to 80 °, with a step length of 0.02.

4.2.3. X-Ray Fluorescence Spectroscopy (XRF)

Elemental composition of the catalyst was analysed with XRF before and after the reaction. The analysis was performed with powder method by using Spectro IQ II instrument and CuK α radiation.

4.2.4. Temperature Programmed Desorption of Ammonia (NH₃-TPD)

The acidity of the catalysts was determined by Temperature-Programmed Desorption of Ammonia (NH₃-TPD) method using Micromeritics AutoChem II Chemisorption Analyzer instrument.

The catalyst samples were heated up to 400 °C by increasing the temperature at a rate of 5 °C/min and kept at this temperature for 30 minutes under He gas flow of 70 ml/min. Then the sample was cooled under He flow of 30 ml/min to 60 °C at a rate of 5 °C/min. This was followed by switching the flow to NH₃-He gas mixture at the rate of 30 ml/min for 30 min. Physically adsorbed NH₃ was removed by degassing the sample at 60 °C under He flow of 70 ml/min for 120 min. NH₃ desorbed sample was analyzed by heating the sample at the rate of 10 °C/min from 60 °C to 700 °C. TCD signal was recorded during the NH₃-TPD.

4.2.5. Skeletal FTIR Spectroscopy

The framework vibration of prepared catalysts which are Ti-SBA-15(10), Ti-SBA-15(20), 8 % MoO₃/Ti-SBA-15(10), 12%MoO₃/Ti-SBA-15(10), 8%MoO₃/Ti-SBA-15(20), 12%MoO₃/Ti-SBA-15(20) were evaluated by FTIR spectroscopy. KBr pellet technique was employed to obtain infrared spectra of the samples at room temperature. The pellets were prepared with a sample amount of 2 mg and sufficient amount of KBr to reach to total amount of 150 mg. The spectra were retrieved in the wavenumber range of 400 - 2000 cm⁻¹ with a resolution of 4 cm⁻¹ by an infrared spectrometer type Shimadzu FTIR 8400S.

4.2.6. Pyridine Adsorbed FTIR

This analysis lead to identify surface Lewis or Bronsted acidic sites. For the analysis, the samples were degassed at 300 °C under vacuum (2×10^{-2} mmHg) for 2 h. Adsorption of pyridine was carried out at 150 °C for 30 minutes. Before FTIR analysis the samples were kept 120 °C under N₂ flow of 30 ml/min for 2 h in order to desorb the physisorbed pyridine. KBr pellets were prepared by pressing a mixture of 2 mg of pyridine adsorbed catalyst sample and 150 mg KBr IR analysis were carried out between 400 and 4000 cm⁻¹ with Shimadzu FTIR 8400S model Fourier Transformed Infrared Spectrometer using KBr pellet technique.

4.3. Characterization of Soybean oil

4.3.1. Gel Permeation Chromatography (GPC)

Number average molecular weight, weight average molecular weight of soybean oil was determined by Gel Permeation Chromatography (GPC). A Shimadzu modular system contains Waters columns, SIL-10AD auto injector, RID-10A refractive-index detector calibrated with narrow PDI of polystyrene. The mobile phase is tetrahydrofuran (THF) with flow rate of 0.3 mL/min.

4.4. Catalytic Tests

4.4.1. Epoxidation of Soybean Oil by Homogeneous Catalyst

In typical procedure of epoxidation by homogeneous catalyst, 87.2 ml of soybean oil, 12.25 ml of acetic acid and 0.39 ml of sulphuric acid were added to reactor and were stirred for 30 min while being heated to 50 °C. After 30 min mixing, 43.03 ml of H₂O₂

solution (35%) was added dropwise for 30 min. After, solution was heated to 65 °C. The reaction duration was 6 h. Samples were collected at 2 h, 4 h and 6 h of reaction time. The collected samples were extracted with diethyl ether in a separating funnel, washed with deionized water to remove free acid. In this reaction, 250 ml of glass reactor was used with condenser. Stirring speed was set to 900 rpm and reaction temperature was 65 °C.

4.4.2. Epoxidation of Soybean Oil by Heterogeneous Catalysts



Figure 4.2. The reactor system for epoxidation of soybean oil

In typical catalytic test for epoxidation reaction, 13.01 ml of soybean oil, 51.73 ml of ethyl acetate and 0.3 g of catalyst were added to the reactor. Stirring speed was set to 900 rpm. For this reaction, 100 ml of three Radley reactors were used with condenser which was in this reactor system which is displayed in Figure 4.2. Each reactor referred to each sample which was taken for different reaction time. After the mixture temperature reached to 60 °C, 4.72 ml of H₂O₂ solution (35%) was added to reaction mixture dropwise and gently. Then, reaction temperature was set as 75°C while being stirred. After adding H₂O₂, three samples were taken in every 2 hour during the reaction time of the 6 h. Collected samples were filtered and washed for 4 times with deionized water. Here, after adding water to reaction mixture, phase separation was observed in the separating funnel. Water and soluble ethyl acetate mixture remained in the bottom part. For separation, this mixture was removed for separation. Therefore, product was separated from the solvent considerably. Then, sodium sulfate was added to samples relatively to remove water in the reaction mixture. After that, remained ethyl acetate in the mixture was

removed keeping in fume cupboard. This was how product samples were taken. For a further study, blank test was carried out without catalyst at the same reaction conditions in terms of same reaction temperature and amount of reactants. Product analysis was applied by same procedure which was mentioned previously.

4.5. Product Analysis

The chemicals which were used in product analysis are given in Table 4.4.

Table 4.4. The chemicals used for product analysis including titrations.

Chemicals	Brand/ Purity
Wij's solution	Fluka, 0.1 M ICI
Potassium iodide	Sigma-Aldrich, $\geq 99,5\%$
Sodium thiosulfate	Sigma-Aldrich, anhydrous, $\geq 98.0\%$
Chloroform	Riedel
Starch solution	Fluka, in saturated salt solution, indicator
HBr solution	Sigma-Aldrich, 30wt.% in acetic acid
Acetic acid	Merck, glacial (100%)
Methyl violet indicator	Sigma-Aldrich
Potassium hydroxide	Sigma-Aldrich
Ethanol	Sigma-Aldrich, absolute, $\geq 99.8\%$
Phenolphthalein indicator	Sigma-Aldrich

4.5.1. Determination of Iodine Value

Iodine value (IV) is used to determine double bonds in fatty acid chains of soybean oil. In other words, it present the degree of unsaturation of oil. This value refers to the grams of absorbed iodine per 100 g of oil. In order to determine iodine value, analytical method such as titration technique was applied. For this purpose, 0.2 g of oil was weighted to a flask. Then, 35 ml of Wijs solution was added to oil and blank flasks. After that, 20 ml of chloroform was added to oil and a blank flask. These two flasks were placed at a dark cupboard for 30 min. After this procedure, 20 ml of %10 potassium iodide solution was added to flasks. Then, 150 ml of deionized water was also added to flasks. The obtained solutions were titrated with 0,1 M sodium thiosulfate solution until straw-yellow colour appeared. Few drops of starch indicator was added to mixtures and titrated again with 0.1 M sodium thiosulfate solution until colourless(like water) appeared. The IV value is determined by using the following equation; (Öktemer et al. 2001)

$$IV = \frac{1.269(V_{\text{blank}} - V_{\text{sample}})}{\text{Weight of sample}} \quad (4.1)$$

Where; IV: iodine value

V_{blank} : titrant volume of blank with no oil.

V_{sample} : titrant volume of sample(oil)

4.5.2. Determination of Acid Value

Acid value (AV) represents the mg of potassium hydroxide in order to neutralize the free acids in 1 g of sample (oil). The following procedure for determination of acid value was as follows. 5 g of sample was weighted to a flask and to which 25 ml of ethanol was added. Then, 5 drops of phenolphthalein solution was added to mixture. For last step, mixture was titrated with 0.1 N KOH solution until purple color appeared and volume that consumed in titration was recorded. Then, acid value was determined by following

equation; (Öktemer et al. 2001)

$$\text{Acid Value (mg of KOH)} = \frac{(\text{ml of KOH}) \times N \times 56}{\text{weight of sample}} \quad (4.2)$$

Where; N: normality of KOH solution

4.5.3. Determination of Oxirane Oxygen Content

Oxirane oxygen content is an important parameter of epoxidized products. This value refers to epoxide content in the product. The following procedure was applied to determine oxirane content of epoxidized soybean oil. 0.1 N HBr solution in acetic acid was prepared. 0.5 g of oil was weighted to flask for analysis. Then, 50 ml of acetic acid was added to sample to dissolve oil. Few drops of methyl violet indicator was added to mixture. After that, mixture was titrated with 0.1 N HBr solution until green colour appeared. The oxirane content was calculated by using following expression; (Öktemer et al. 2001)

$$\text{Oxirane Content (\%)} = \frac{\text{VHBR} \times 0.1 \times 1.6}{\text{weight of sample (g)}} \quad (4.3)$$

4.5.4. Fourier-Transform Infrared Spectroscopy (FTIR)

Functional groups of synthesized epoxidized samples were investigated by FTIR spectroscopy. All measurements were carried out by using KBr pellet technique at room temperature. The pellets were prepared with 150 mg KBr. The liquid samples are dropped and spreaded on pellets and epoxide products in liquid form are analyzed separately. IR analysis were carried out between 400 and 4000 cm^{-1} with Shimadzu FTIR 8400S model Fourier Transformed Infrared Spectrometer. Characteristic IR bands associated with soybean oil and epoxidized soybean oil are displayed in Table 4.3. FTIR spectra of the obtained epoxidized soybean oils were evaluated by using this table.

Table 4.5. Characteristic IR bands associated with soybean oil and epoxidized soybean oil. (Source: Sienkiewicz et al. 2016)

Band	Frequency [cm ⁻¹]	Oil associated band
1	3009	—C—H (next to double) band stretching
2	2926	—CH ₂ asymmetric stretching
3	2855	—CH ₃ symmetric stretching
4	1746	—C=O stretching
5	1655	—C=C stretching
6	1465	—CH ₂ stretching
7	1418	—C=C—H deformational
8	1378	—CH ₃ symmetric deformational
9	843	—C—O—C— epoxy group stretching
10	723	—CH ₂ oscillating

4.5.5. Proton Nuclear Magnetic Resonance Spectroscopy (H-NMR)

NMR analysis was carried out by a Varian Inova 300 MHz spectrometer in order to observe magnetic fields around atomic nuclei. It is used to determine unique structure of compounds. For this analysis, epoxidized samples were dissolved in deuterated chloroform (CDCl₃) as a solvent that contains tetramethylsilane (TMS) as an internal standard. Before NMR analysis, epoxidized soybean oil sample was taken as 60μl. This sample was dissolved in 0,5 ml of deuterated chloroform.

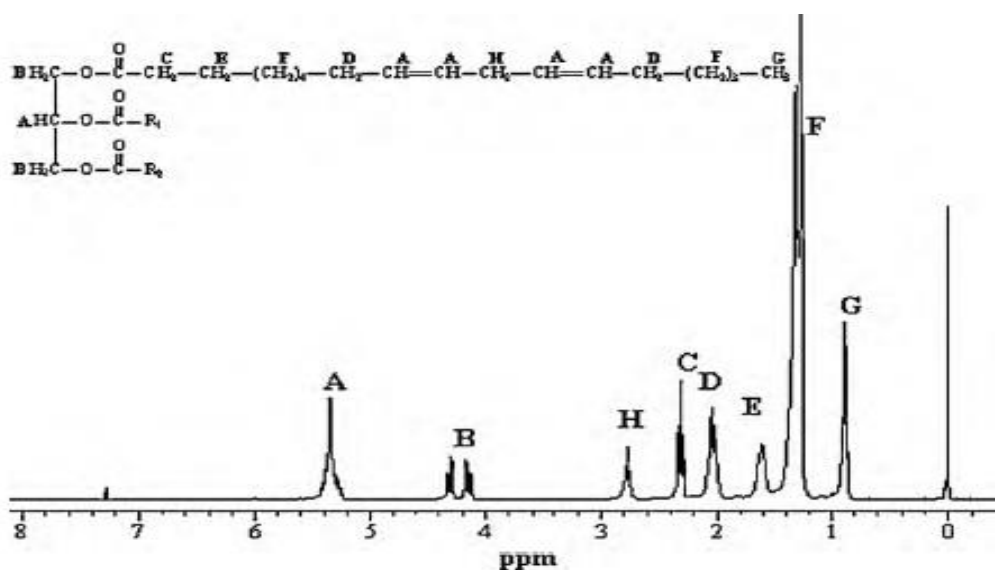


Figure 4.3. H-NMR spectrum of original soybean oil sample (Source: Farias et al. 2010)

Quantitative analysis can be performed by NMR technique. Some equations related to peak areas associated with special part were used for calculations. Necessary equations for quantitative analysis are given below(Farias et al 2010).

$$NF = \frac{B}{4} \quad (4.4)$$

NF; is the normalisation factor, B; is the area of the signal associated with the four hydrogens of the methylene groups of the glycerol moiety.

$$NDi = \frac{A - NF}{2NF} \quad (4.5)$$

NDi; the number of double bonds in the original soybean oil

$$M = \frac{15.034G}{3NF} + \frac{14.026(C + D + E + F + H)}{2NF} + \frac{26.016(A - NF)}{2NF} + 173.1 \quad (4.6)$$

M; mean molecular weight of the sample(soybean oil)

C, D, E, F, H; the peak areas associated with the methylene hydrogens of the triglyceride

G; the peak area of the methyl hydrogens of the triglyceride

A; the peak area of the olefinic hydrogens plus the peak area of the methine hydrogen of the glycerol moiety (Farias et al. 2010).

$$Conversion (\%) = \frac{NDi - NDf}{NDi} \times 100 \quad (4.7)$$

$$Epoxidation(\%) = \frac{(I + J) \div 2}{NF \times NDi} \times 100 \quad (4.8)$$

$$Selectivity (\%) = \frac{Epoxidation(\%)}{Conversion(\%)} \times 100 \quad (4.9)$$

I, J; the peak areas associated with the hydrogens of the epoxide groups at chemical shifts of 2.9 ppm (monoepoxide) and 3.1 ppm (diepoxide), separately.

CHAPTER 5

RESULTS AND DISCUSSION

5.1. Characterization of Catalysts

In the characterization part, textural properties of the catalysts, elemental composition, acidity were determined. The catalysts labels are tabulated below.

Table 5.1. Notations of the prepared catalysts

Catalysts	Labels of Prepared Catalysts
Ti-SBA-15 (Si/Ti=10)	TSB10
Ti-SBA-15 (Si/Ti=20)	TSB20
% 8 MoO ₃ / Ti-SBA-15 (Si/Ti=10)	8MTSB10
% 12 MoO ₃ / Ti-SBA-15 (Si/Ti=10)	12MTSB10
% 8 MoO ₃ / Ti-SBA-15 (Si/Ti=20)	8MTSB20
% 12 MoO ₃ / Ti-SBA-15 (Si/Ti=20)	12MTSB20

The crystal structure of TSB10, 8MTSB10 and 12MTSB10 were examined by X-Ray Diffraction analysis. The patterns of these catalysts are displayed in Figure 5.1. According to the obtained patterns, diffraction peaks at 25.5, 38, 48.5, 55 referred to anatase phase of titanium while diffraction peak at 29 were related to MoO₃.

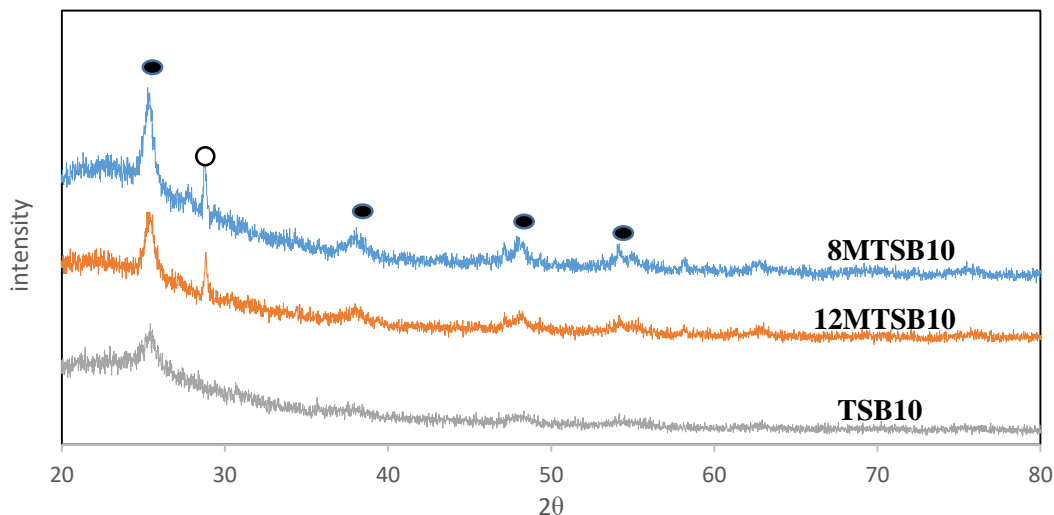


Figure 5.1. XRD patterns of TSB10, 8MTSB10 and 12MTSB10; (•) anatase phase of TiO_2 , (o) MoO_3 .

In the same way, the crystal structure of TSB20, 8MTSB20 and 12MTSB20 were examined by X-Ray Diffraction analysis. The patterns of these catalysts are displayed in Figure 5.2. Similar to previous patterns, diffraction peaks at 25.5, 38, 48.5, 55 referred to anatase phase of titanium but peaks did not appear as distinct as observed for TSB10 catalyst. Peak at 29 was related to MoO_3 crystal on the catalyst surface.

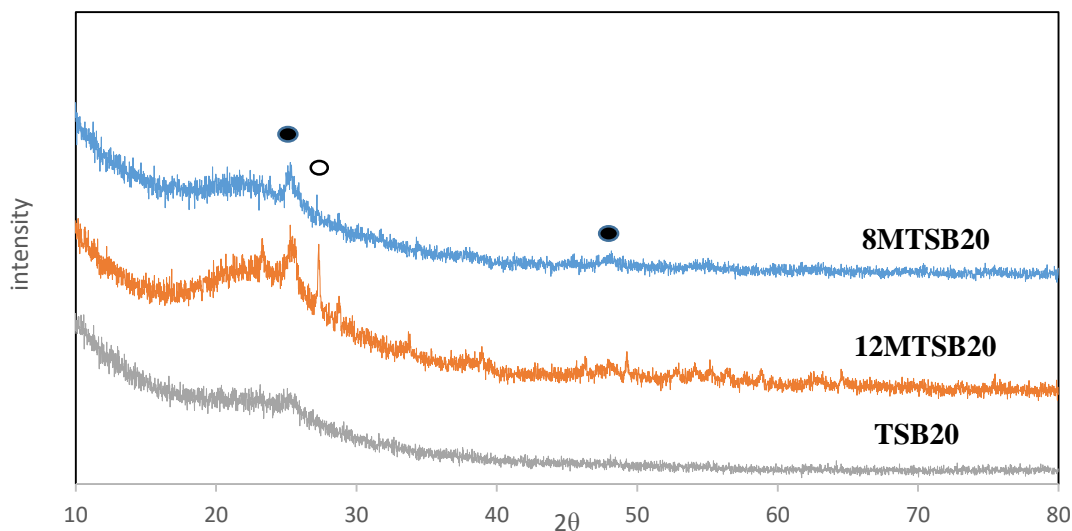


Figure 5.2. XRD patterns of TSB20, 8MTSB20 and 12MTSB20; (•) anatase phase of TiO_2 , (o) MoO_3 crystal.

Figure 5.3 displays N_2 adsorption-desorption isotherm of 8MTSB10 and 8MTSB20 catalysts. These catalysts indicated the type IV adsorption isotherm with a

hysteresis loop. Position of the hysteresis loop at high relative pressure indicates the presence of mesoporous channels in these catalysts. The textural properties such as surface area, pore volume and pore diameter were determined by N₂ adsorption analysis. These properties of the catalysts are given in Table 5.2, respectively. The surface area decreased with MoO₃ loading, pore volume also decreased very little with MoO₃ loading. However, pore diameter increased with MoO₃ loading on the contrary to surface area and pore volume. Furthermore, it was found that with increase in Si/Ti ratio the surface area increased. The pore diameter and pore volume increased with increasing Si/Ti ratio.

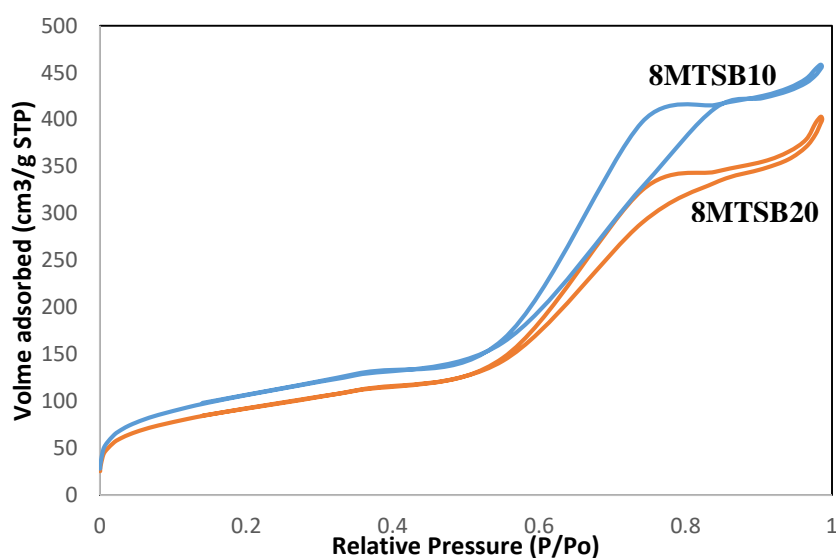


Figure 5.3. N₂ adsorption-desorption isotherm of 8MTSB10 and 8MTSB20 catalysts.

Table 5.2. Textural properties of the prepared catalysts.

CATALYST	SURFACE AREA (m ² /g)	PORE DIAMETER (Å)	PORE VOLUME (cm ³ /g)
TSB10	856.11	45.1	0.594
8MTSB10	328.93	60.5	0.576
12MTSB10	347.35	57.4	0.560
TSB20	913.60	45.9	0.677
8MTSB20	378.44	59.9	0.655
12MTSB20	362.52	60.4	0.627

The elemental analysis of the catalysts were determined by XRF analysis. The elemental compositions of the catalysts are demonstrated in Table 5.3. This gave information about contents, additionally provided to check the loading amount or molar ratio contents. According to table given below, elemental composition of the catalysts proved the molar ratio which were similar with the synthesis procedure. However, MoO₃ loading was not in 12MTSB20 as it was expected. There can be experimental mistakes during impregnation procedure.

Table 5.3. Elemental analysis of the prepared catalysts.

CATALYSTS	Ti(%)	Si(%)	Mo(%)
Ti-SBA-15(Si/Ti=10)	5.45	42.11	
% 8 MoO ₃ / Ti-SBA-15(Si/Ti=10)	4.58	42.24	1.09
% 12 MoO ₃ / Ti-SBA-15(Si/Ti=10)	4.32	41.6	2.043
Ti-SBA-15(Si/Ti=20)	2.79	44.21	
% 8 MoO ₃ / Ti-SBA-15(Si/Ti=20)	2.25	43.95	1.23
% 12 MoO ₃ / Ti-SBA-15(Si/Ti=20)	2.24	43.46	1.24

The framework vibration of TSB10, 8MTSB10 and 12MTSB10 are investigated by Fourier Transform Infrared Spectroscopy. This technique presented the nature of Ti in the silica based framework. The spectra of these catalysts are demonstrated in Figure 5.4. It was found that the band range at 910-960 cm⁻¹ was due to Si-O-Ti vibration. The band in the range of 3700-3000cm⁻¹ was because of the evidence of surface hydroxyl group

and physisorbed water. (Sharma et al. 2012). Generally, anatase phase of titanium appeared the band in $850\text{-}650\text{ cm}^{-1}$.

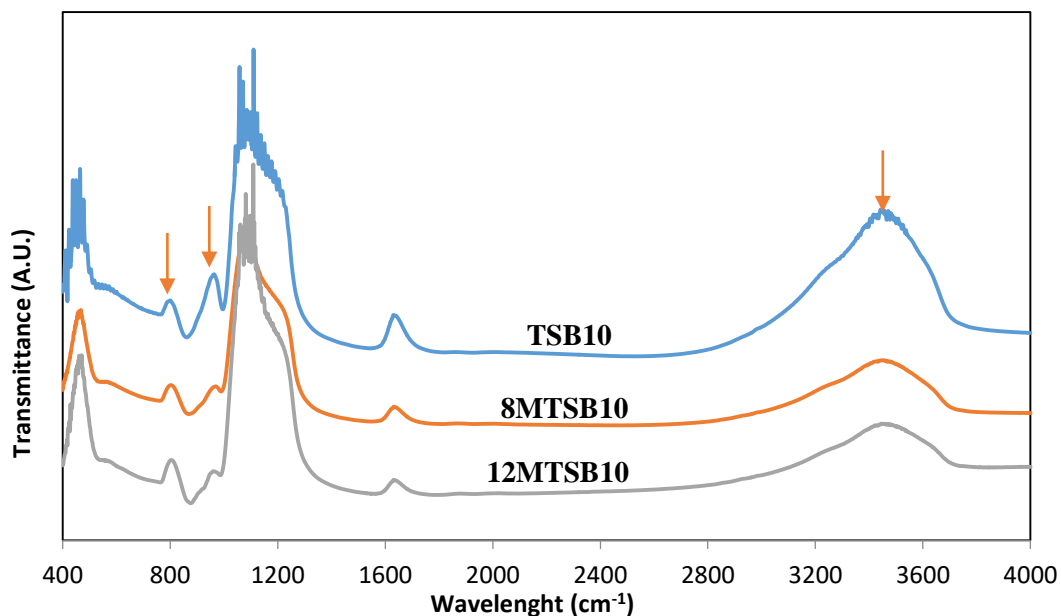


Figure 5.4. Skeletal FTIR spectra of TSB10, 8MTSB10 and 12MTSB10 catalysts.

The spectra of TSB20, 8MTSB20 and 12MTSB20 catalysts are demonstrated in Figure 5.5. The framework vibration of TSB20, 8MTSB20 and 12MTSB20 are investigated by Fourier Transform Spectroscopy. The band range at $910\text{-}960\text{ cm}^{-1}$ was due to Si-O-Ti vibration. The band in the range of $3700\text{-}3000\text{ cm}^{-1}$ was because of the evidence of surface hydroxyl group and physisorbed water (Sharma et al. 2012).

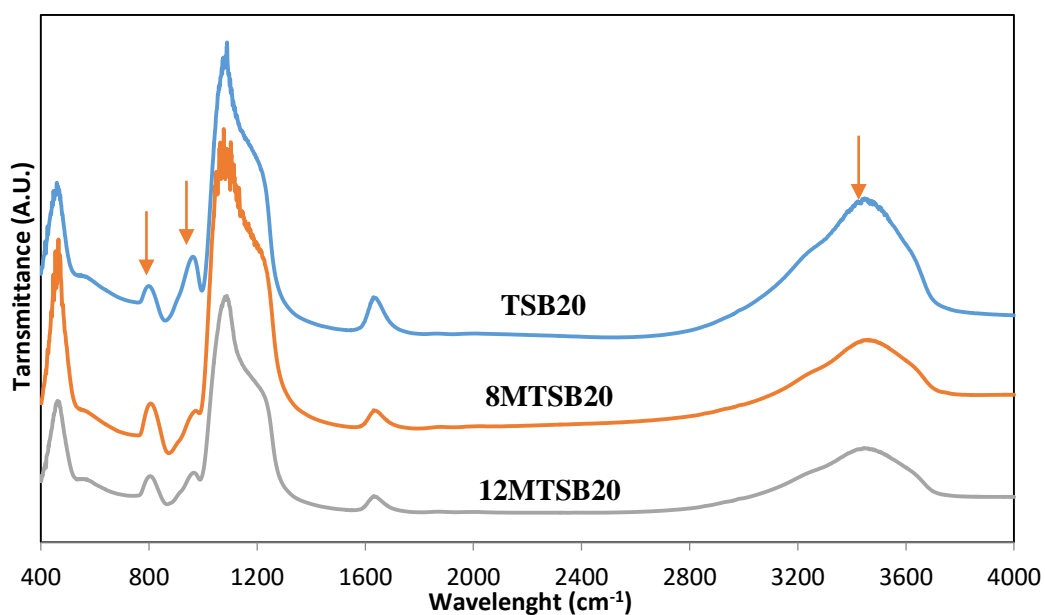


Figure 5.5. Skeletal FTIR spectra of TSB20, 8MTSB20 and 12MTSB20 catalysts

The acidity of TSB10, TSB20, 8MTSB10, 12MTSB10 and 12MTSB20 catalysts were examined by using NH₃-TPD. The results are given in Figure 5.6. Generally, peaks are categorized by two main groups as high temperature region ($T > 400$ °C) and low temperature region ($T < 400$ °C) in NH₃-TPD profiles. Peaks that are related to high temperature region, revealed to desorption of ammonia from strong Bronsted and Lewis acid sites. Peaks in low temperature region are inferred to desorption of ammonia from weak acid sites. TSB10 and TSB20 catalysts exhibited one peak in the low temperature range. This peak was related to free hydroxyl group on the surface of the catalysts. Furthermore, this peak represented to weak acid sites. The acidities of these two catalysts were similar. The acidity of TSB20 catalyst was slightly higher. This could be due to higher Si/Ti ratio.

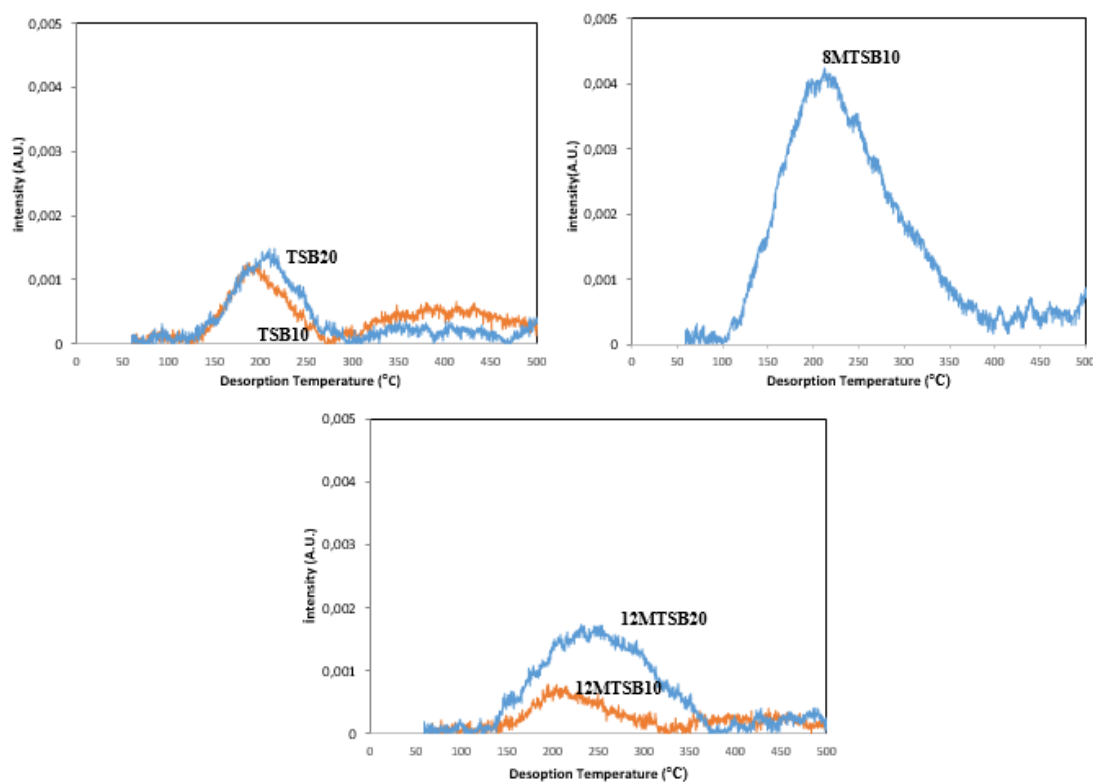


Figure 5.6. NH₃-TPD profiles of TSB10, TSB20, 8MTSB10, 12MTSB10 and 12MTSB20 catalysts.

8MTSB10 catalyst exhibited one broad peak in the range of 105-394 °C. This presented the weak to medium acid strength. Loading Mo increased acid sites significantly. There was one peak in the low temperature region for profiles of both catalysts. The acidity of 12MTSB20 was higher than that of 12MTSB10. The lower Mo loading provided higher acidity of catalyst.

FTIR spectra of pyridine adsorbed material indicates acid types of the material. The acid types of TSB10 and TSB20 are demonstrated in Figure 5.9. When pyridine interacts with surface Brønsted acid sites, the presence of the pyridinium species is presented by adsorption bands at 1540 and 1640 cm^{-1} (Sharma et al. 2014).

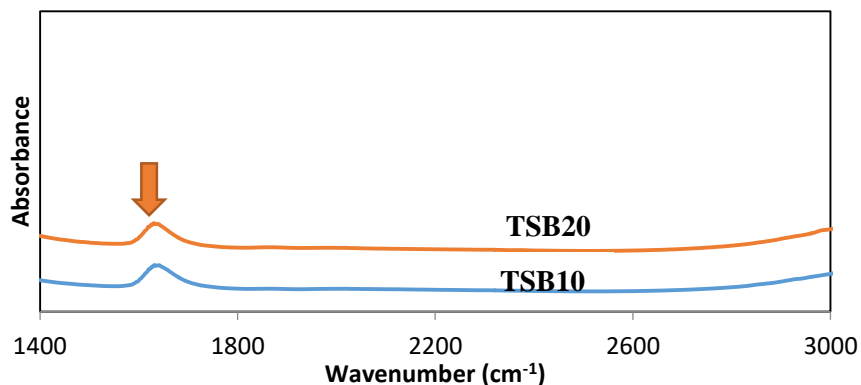


Figure 5.7. FTIR spectra of pyridine adsorbed TSB10 and TSB20 catalysts.

5.2. Characterization of Soybean Oil

The number average molecular weight and weight average molecular weight of soybean oil were determined by Gel Permeation Chromatography (GPC). The number average molecular weight of soybean oil was found as 945 and the weight average molecular weight of soybean oil was obtained as 973. The polydispersity index (PDI) was calculated as 1.03. The polydispersity index presents the broadness of molecular weight distribution.

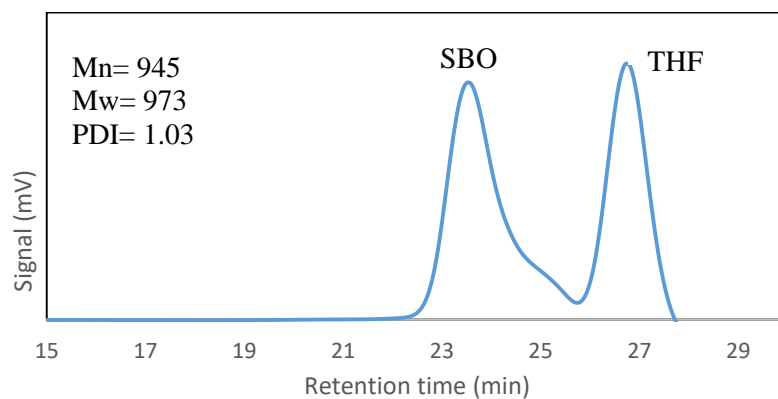


Figure 5.8. GPC Chromatogram of soybean oil.

5.3. Catalyst Testing

5.3.1. Epoxidation of Soybean Oil by Homogeneous Catalyst

FTIR spectra of the epoxidized soybean oil produced by H_2SO_4 are given in Figure 5.9. The bands at 3009 cm^{-1} and 1656 cm^{-1} with little peaks are related to double bonds. The peak of double bonds are expected to decrease because its conversion. These peaks decreased for increasing reaction time as it was expected. The band at 824 cm^{-1} which shows oxirane group, was appeared significantly. H_2SO_4 was active in epoxidation reaction.

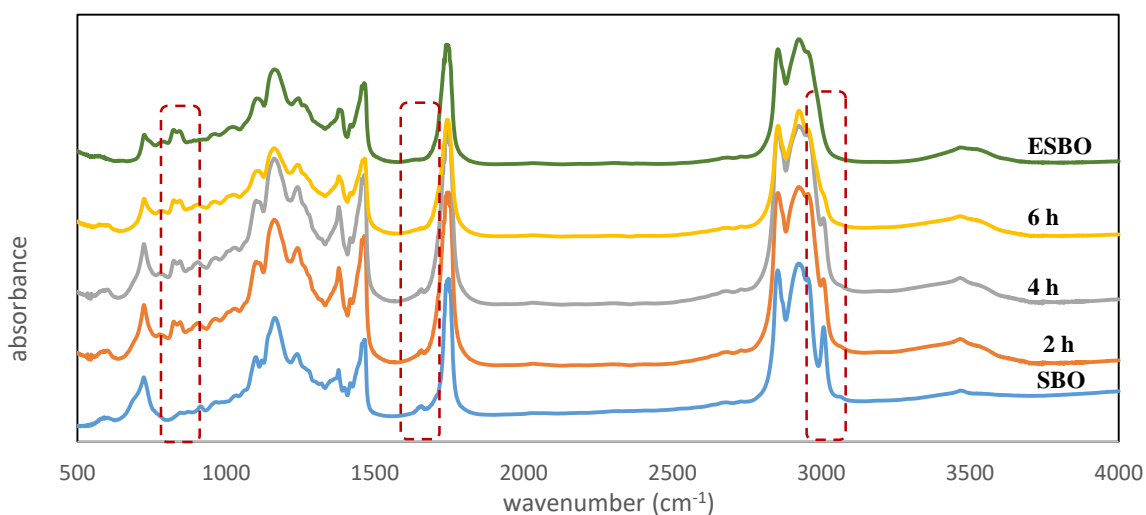


Figure 5.9. FTIR spectra of soybean oil, epoxidized soybean oil (commercial) and epoxidized soybean oil with H_2SO_4 for 2, 4 and 6 h.

The NMR spectra of soybean oil is shown in Figure 5.19. The spectrum of soybean oil were exhibited in order to compare and evaluate the spectrum of the products.

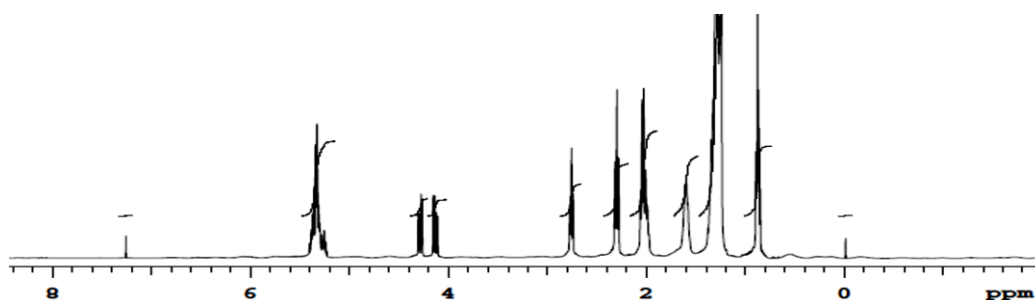


Figure 5.10. H-NMR spectrum of soybean oil

NMR spectra of epoxidized soybean oil samples obtained with H_2SO_4 catalyst are given in the Figure 5.11. These products were taken at 2, 4, 6 h of reaction time. The peaks in the range of 2.9 - 3.1 ppm were indicated epoxy groups in the products. These peaks were observed for all the products taken at different reaction time. This result was in agreement with the literature about the epoxidation reaction in the presence of mineral acid as a catalyst (Benaniba et al. 2007 and Farias et al. 2010). It can be seen that the peak areas changed with reaction time.

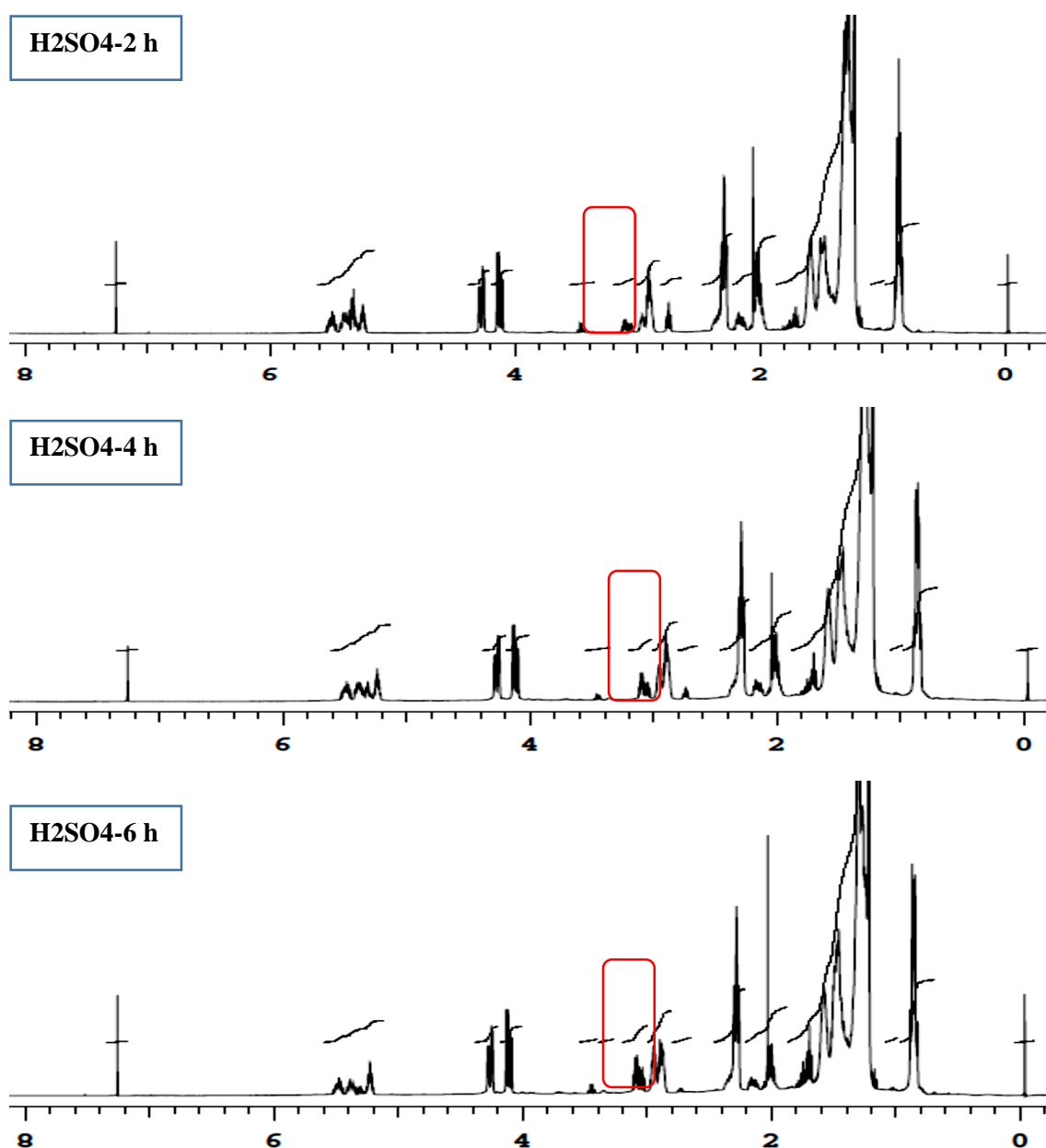


Figure 5.11. NMR spectra of epoxidized soybean oil by H_2SO_4 after 2, 4, 6 h reaction time.

The results of soybean oil conversion ($X_{sbo}\%$), epoxidation (Epoxy%) and selectivity to epoxidized soybean oil ($S_{epoxy}\%$) are given in Table 5.6. These results were obtained by using equation of 4.7, 4.8 and 4.9. These findings were obtained from NMR results of epoxidized soybean oil with H_2SO_4 . $X_{sbo}\%$ and Epoxy% increased with increasing reaction time. The selectivity increased but after 4 h decreased slightly. The highest conversion of soybean oil was found as 78.2 %. The highest epoxidation was obtained as 71.2% and the highest selectivity was found as 94.3 %. These values are good results as it was expected for homogeneously catalyzed epoxidation reaction.

Table 5.6. Soybean oil conversion, epoxidation and selectivity to epoxide with H_2SO_4 catalyst for different reaction time.

Catalyst	Reaction time (h)	$X_{SBO}\%$	Epoxy%	$S_{epoxy}\%$
H_2SO_4	2	55.4	52.2	94.0
H_2SO_4	4	70.0	66.0	94.3
H_2SO_4	6	78.2	71.2	91.0

5.3.2. Epoxidation of Soybean Oil by Heterogenous Catalysts

The FTIR spectra of soybean oil epoxidized over TSB10, 8MTSB10 and 12MTSB10 catalysts for different reaction time are shown in Figures 5.12 to 5.14. The samples of the soybean oil epoxidized were taken at 2, 4 and 6 h of reaction time. The soybean oil epoxidized from the reaction were compared with commercial soybean oil and soybean oil epoxidized that was supplied from the industry. These spectrums displayed that bands at 3009 and 1650 cm^{-1} presented characteristic unsaturated bonds namely, C=C double bonds in the fatty acid chains of oils. These bands were expected to disappear or decrease because of their conversion to epoxy groups. Addition to these, the band at 824 cm^{-1} referred to epoxy group that was also called oxirane group. It can be seen that these bonds had very little intensities, therefore they were not appropriate to evaluate the performance of the catalyst. These results indicated that the catalysts showed low activity in soybean oil epoxidation.

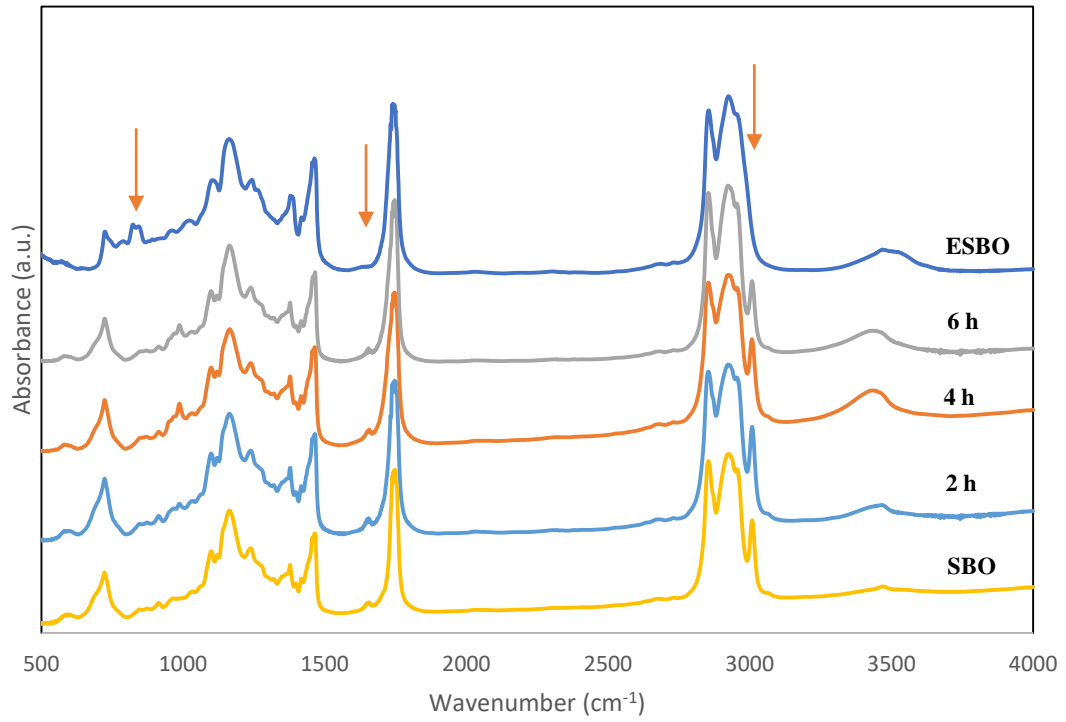


Figure 5.12. FTIR spectrum of products obtained from soybean oil epoxidation over TSB10.

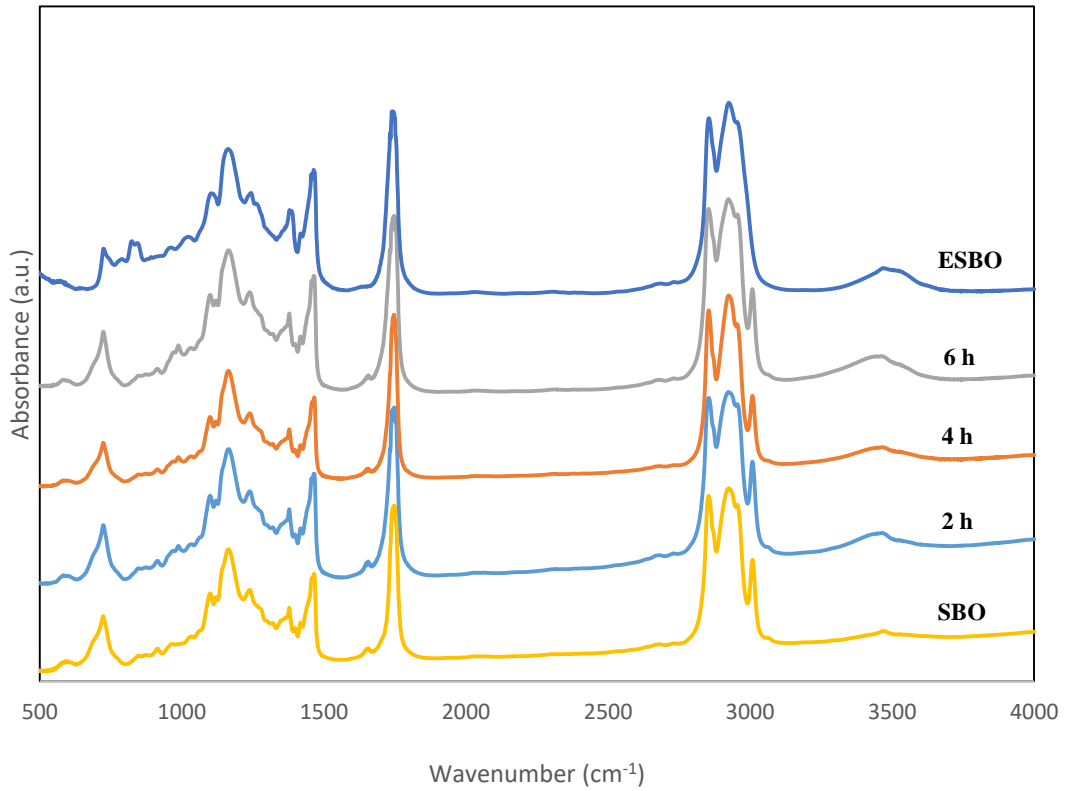


Figure 5.13. FTIR spectrum of products obtained from soybean oil epoxidation over 8MTSB10.

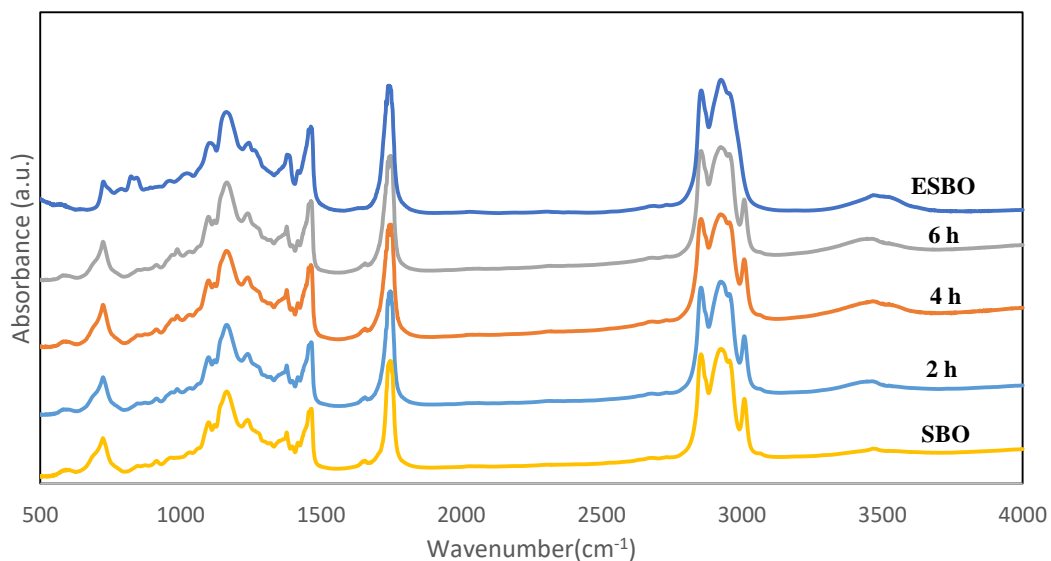


Figure 5.14. FTIR spectrum of products obtained from soybean oil epoxidation over 12MTSB10.

The FTIR spectra of products obtained from soybean oil epoxidation over TSB20, 8MTSB20 and 12MTSB20 are demonstrated in Figures 5.15 to 5.17. The products taken at 2, 4, 6 h were analyzed. The bands at 3009 and 1650 cm^{-1} which were related to double bonds decreased very little. Moreover, when evaluated the band at 824 cm^{-1} , increase in absorbance values of these bands were not observed properly for TSB20 catalyst. Because, increase in absorbance was little. These peaks for 8MTSB20 and 12MTSB20 were appeared a little bit larger.

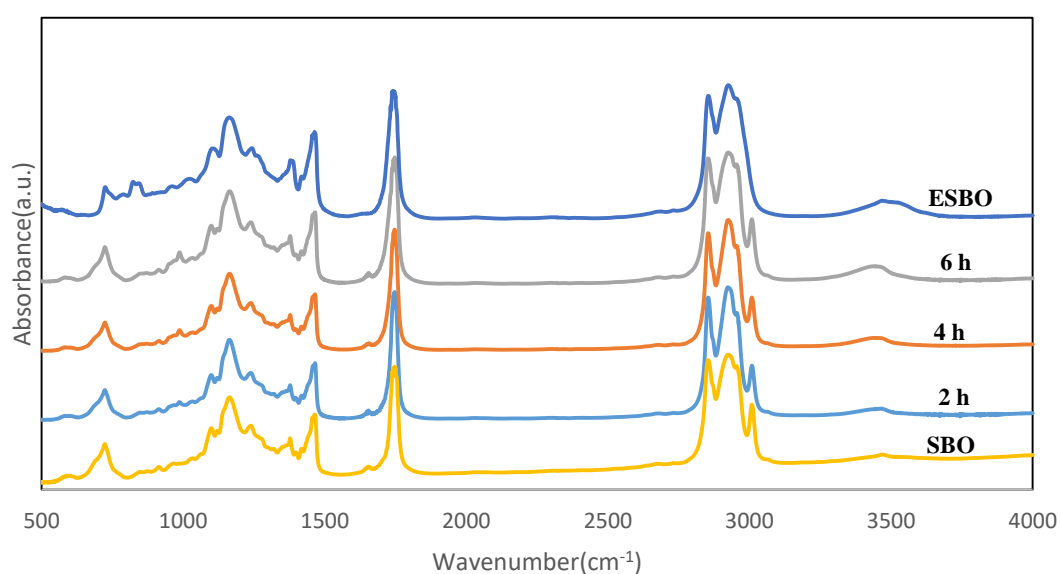


Figure 5.15. FTIR spectrum of products obtained from soybean oil epoxidation over TSB20.

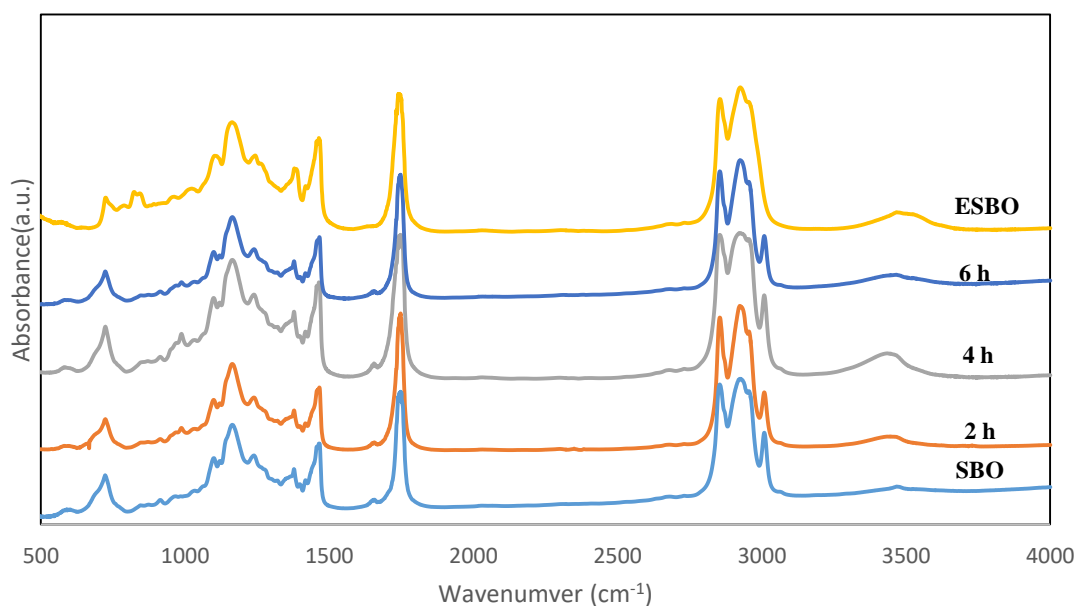


Figure 5.16. FTIR spectrum of products obtained from soybean oil epoxidation over 8MTSB20.

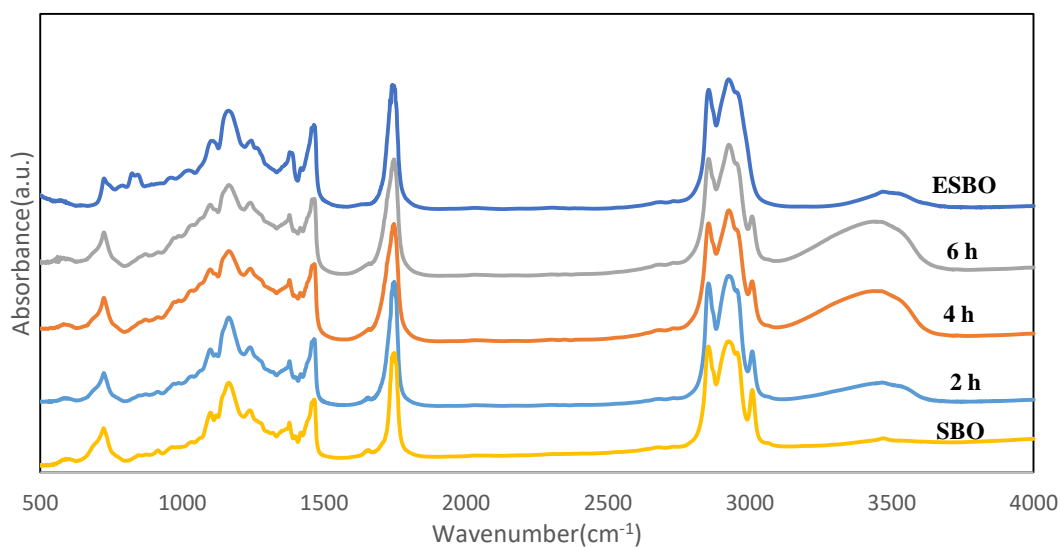


Figure 5.17. FTIR spectrum of products obtained from soybean oil epoxidation over 12MTSB20.

The spectrum of epoxidized soybean oil over TSB10 for 6 h of reaction time is given in Figure 5.20. Peak at 2.9 ppm showed the epoxy group that formed after epoxidation of soybean oil. The peak was not large. But this was considered as acceptable result because when compared to results of another studies in the literature, this peak was expected in terms of our selected reaction time (6 h). In other words, other studies carried out longer reaction time which reached to almost 57 h. Therefore, this epoxy peak can be considered as an expectable outcome.

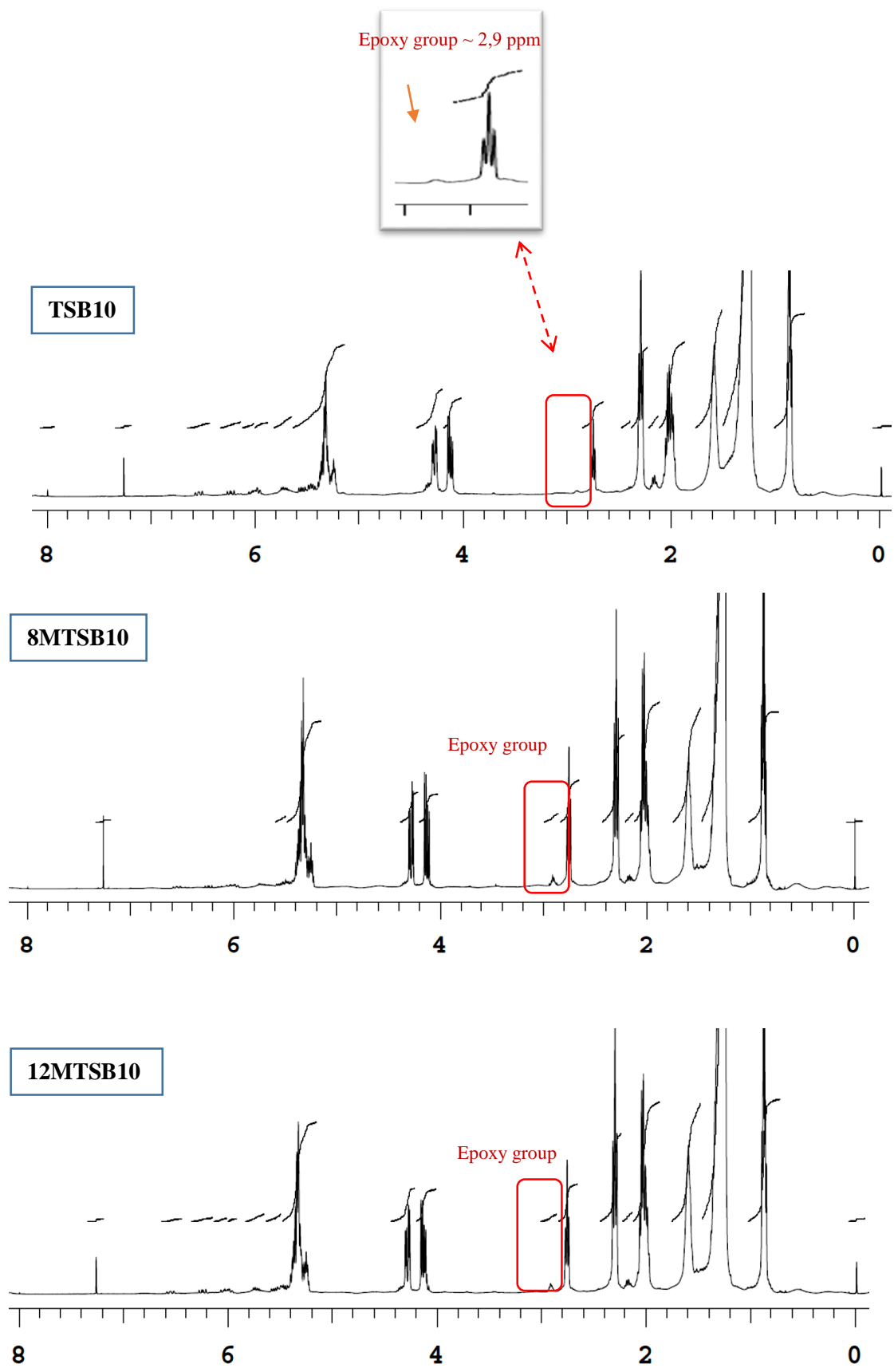


Figure 5.18. H-NMR spectra of epoxidized soybean oil over TSB10, 8MTSB10 and 12MTSB10 at 6 h reaction time.

The spectra of epoxidized soybean oil with TSB10, 8MTSB10 and 12MTSB10 for 6 h of reaction time are presented in Figure 5.18. Similar to figure above, signal at 2.9 ppm expressed the epoxy group on the epoxidized soybean oil. These two peaks were much larger than that with TSB10. Hence, it was considered that MoO₃ loaded catalysts were more active and selective catalysts. The peak area for 8MTSB10 was greater than that of 12MTSB10.

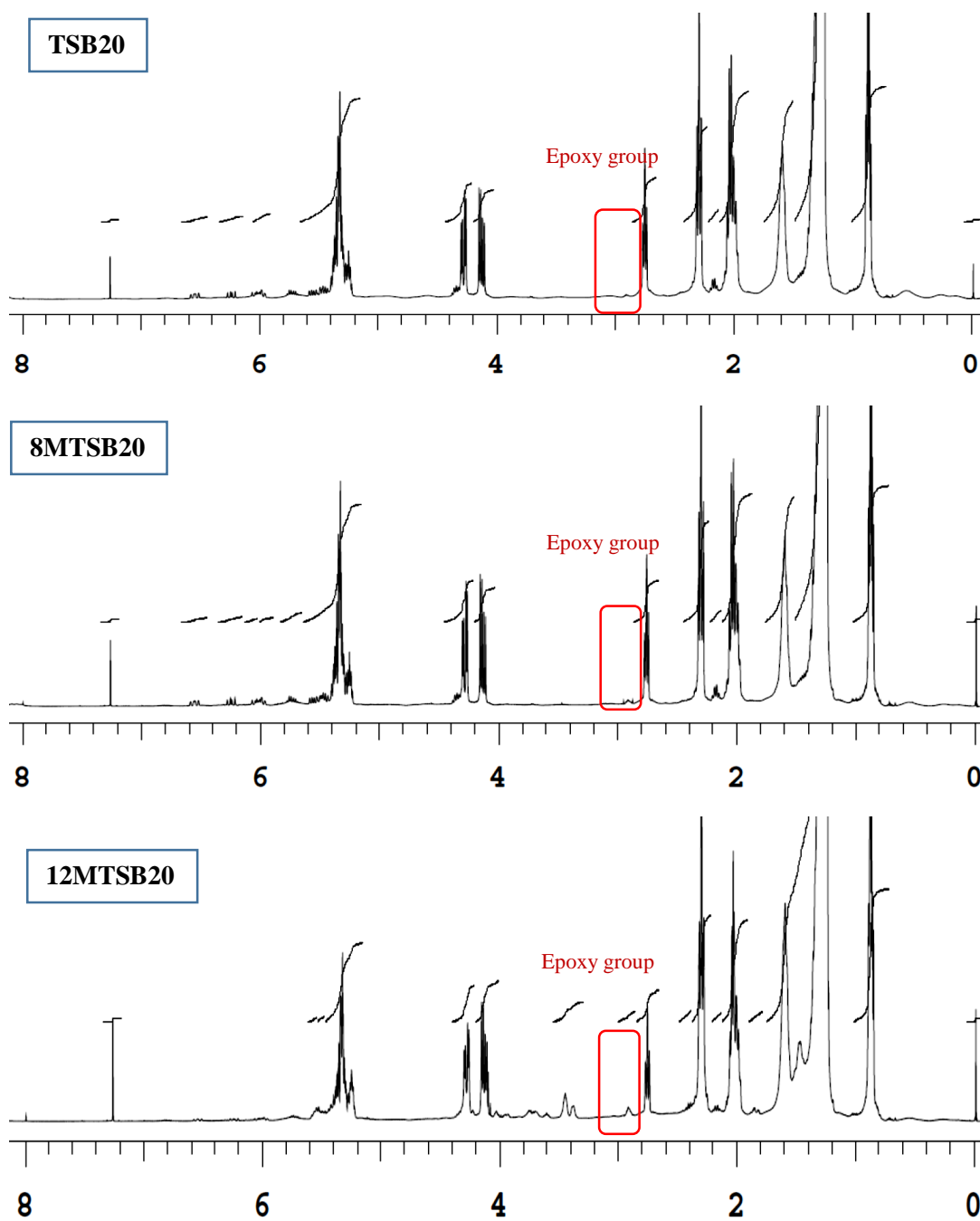


Figure 5.19. H-NMR spectra of soybean oil epoxidation products over TSB20, 8MTSB20 and 12MTSB20 for 6 h of reaction time.

Figure 5.19 displays the spectrum of soybean oil epoxidation products over TSB20 based catalysts at 6 h of reaction time. A small epoxy peak was observed at 2.9 ppm which was similar to peak which obtained in epoxidized soybean oil by TSB10. This peak also had smaller area compared to the products obtained over 8MTSB10 and 12MTSB10 catalysts.

To make quantitative analysis with NMR spectra of the products, peak areas were used to determine conversion, epoxidation and selectivity. This calculation was applied to the soybean oil epoxidation products taken at 6 h reaction time. The results from these calculations are tabulated in Table 5.7. Soybean oil conversion over TSB10, 8MTSB10 and 12MTSB10 as function of reaction time are increased, they do not increase steadily. Conversion with TSB10 increased with reaction time. Conversions with 8MTSB10 for 2 h and 4 h were almost same and when reaction time reached to 6 h, conversion increased a little bit. Therefore, this catalyst deactivated during the reaction time. Conversion with 12MTSB10 increased up to 4 h, but remained almost same value at 6 h. This behavior implied that the catalyst also deactivated.

Taking into consideration epoxidation (Epoxy %) with TSB10, 8MTSB10 and 12MTSB10 catalysts, epoxidation of all catalysts increased with increasing reaction time slightly. 8MTSB10 gave the highest epoxidation as 9.9 % among these three catalysts. However, 12MTSB10 obtained greatest selectivity to epoxide value as 33.9 %, this value was near to that of 8MTSB10. While selectivity decreased with increasing reaction time for TSB10 catalyst, this implied that other products formed with time. Among these catalysts 8MTSB10 was promising in terms of activity and selectivity.

Table 5.7. Soybean oil conversion, epoxidation and selectivity to epoxide determined from H-NMR results.

Catalyst	Reaction time(h)	X_{SBO}%	Epoxy%	S_{epoxy}%
TSB10	2	7.7	4.0	51.9
	4	28.0	5.2	18.6
	6	33.8	7.7	22.8
8MTSB10	2	24.5	6.3	25.7
	4	24.5	8.5	34.0
	6	31.0	9.9	31.9
12MTSB10	2	16.5	3.6	21.8
	4	25.6	9.0	35.0
	6	25.9	8.8	33.9

Table 5.8 displays soybean oil conversion, epoxidation and selectivity to epoxide over TSB20, 8MTSB20 and 12MTSB20 catalysts for different reaction time. Conversion increased with reaction time for 8MTSB20 and 12MTSB20 catalysts. TSB20 catalyst deactivated during the reaction time. 12MTSB20 provided the highest conversion value as 50.2% for 6 h of reaction time. But its selectivity was the smallest value among them. That's why, it can be said that 12MTSB20 was not selective catalyst for epoxidation of soybean oil. The highest selectivity was obtained as 40.7% with TSB20 but conversion was the lowest for 6 h. Selectivity to epoxide increased with increasing reaction time over 8MTSB20 reached 35.6%. The changes in selectivity to epoxides was attributed to formation of other products.

From two group of catalysts (TSB10 and TSB20 based), 8 % molybdenum loading (8MTSB10 and 8 MTSB20) provided gave the best performance in terms of activity and selectivity to epoxide. This showed that low loading of molybdenum was better. In addition, higher Si/Ti ratio enhanced activity and selectivity.

Table 5.8. Soybean oil conversion, epoxidation and selectivity to epoxide determined from H-NMR results.

Catalyst	Reaction time(h)	X_{SBO}%	Epoxy%	S_{epoxy}%
TSB20	2	10.3	2.0	19.4
	4	10.7	2.4	22.4
	6	13.0	5.3	40.7
8MTSB20	2	15.0	2.5	16.7
	4	21.5	3.7	17.2
	6	35.6	7.6	35.6
12MTSB20	2	32.3	8.8	27.2
	4	38.2	10.7	28.0
	6	50.2	8.1	16.2

Iodine value and oxirane content of the epoxidized soybean oil samples after 6 h reaction with different catalysts are given in Table 5.9. These values were determined by analytical methods which included titration technique. At the same time, the products from blank experiment were evaluated by this method. The iodine value of the soybean oil was 136 and it dropped to 114.2 in the blank test (no catalyst). This showed that at reaction conditions there was conversion of oil without any catalyst.

Iodine value of soybean oil which was used in epoxidation reaction is 136 g I₂/100 g oil. Its value changed differently with the catalyst used. The lowest iodine value was found as 60.2 with 12MTSB20 which showed the highest conversion obtained as found from NMR analysis. For the other catalysts, it changed between 80.5 and 89.4. The highest oxirane content was found as 0.78 with 8MTSB10. The smallest oxirane content was obtained as 0.32 with no catalysts (blank experiment). Furthermore, acid value of epoxidized soybean oil with 8MTSB10 was found as 3.3. Acid values of other samples were not calculated because of being not enough.

Table 5.9. Iodine value, oxirane content of the products at 6 h.

Catalyst	Iodine Value (g I₂/100 g oil)	Oxirane content
No catalyst	114.2	0.32
TSB10	80.9	0.6
TSB20	102.5	0.39
8MTSB10	89.4	0.78
12MTSB10	87.0	0.62
8MTSB20	88.5	0.58
12MTSB20	60.2	0.63

Combining findings from NMR and titration method, 8MTSB10 catalyst can be considered as the most promising catalyst found in the present study. This could be related to its high acidity compared to other catalysts.

Figure 5.20 displays the epoxidized soybean oil products over the prepared catalysts. They looked yellowish liquid like a clear oil form.

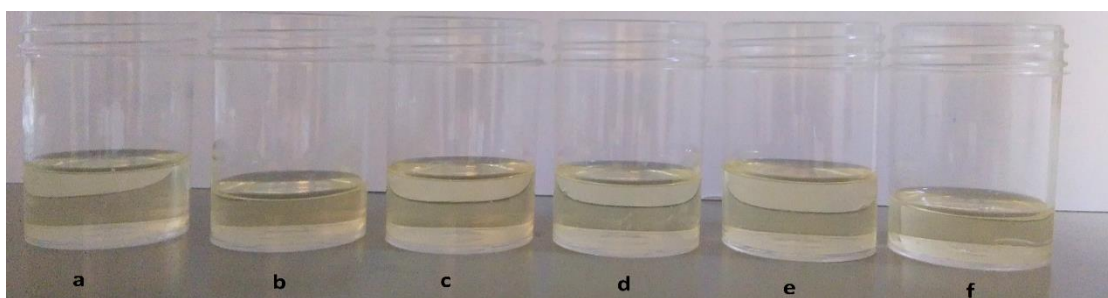


Figure 5.20. Epoxidized soybean oil samples over; (a) ESBOTSB10, (b) ESBO8MTSB10, (c) ESBO12MTSB10, (d) ESBOTSB20, (e) ESBO8MTSB20, (f) ESBO12MTSB20.

CHAPTER 6

CONCLUSION

Mesoporous Ti-SBA-15 and MoO₃/Ti-SBA-15 catalysts were prepared. Ti was in anatase phase. Increasing titania content did not change acidity of the catalysts (TSB10 and TSB20). Mo loading increased the acidity of the catalysts significantly. However, it decreased surface area of the catalysts.

The catalyst activities and selectivity to epoxide changed depending on the acidity of the catalysts. Some of the catalysts namely TSB10, 12MTSB10 and TSB20 deactivated during the reaction. The reason for this was not clear.

Higher activities and selectivities were observed over more acidic catalysts. The most active and selective catalyst was found to be 8MTSB10 catalyst.

REFERENCES

- Abdullah, BM, J. Salimon. "Epoxidation of Vegetable Oils: Catalysts, Methods and Advantages". *Journal of Applied Sciences*. 10.15 (2010):1545-1553.
- Benaniba, Mohamed Tahar, Naima Belhaneche-Bensemra, and Georges Gelbard. "Kinetics of tungsten-catalyzed sunflower oil epoxidation studied by ¹H NMR." *European journal of lipid science and technology*.10.12 (2007): 1186-1193.
- Campanella, A, MA. Baltanas, MA. Capel-Sanchez. "Soybean oil epoxidation with hydrogen peroxide using an amorphous Ti/SiO₂ catalyst". *Green Chemistry*, 6 (2004):330-334.
- Danov, S. M., O. A Kazantsev, A. L. Esipovich, A. S. Belousov, A. E. Rogozhin, & E. A. Kanakov. "Recent advances in the field of selective epoxidation of vegetable oils and their derivatives: a review and perspective". *Catalysis Science & Technology*, 7.17 (2017): 3659-3675.
- Dinda, S. , A. V. Patwardhan, V. V. Goud, & N. C. Pradhan. " Epoxidation of cottonseed oil by aqueous hydrogen peroxide catalysed by liquid inorganic acids". *Bioresource Technology*, 99.9 (2008):3737-3744.
- Farias, M., M. Martinelli, and D.P. Bottega. "Epoxidation of soybean oil using a homogeneous catalytic system based on a molybdenum (VI) complex." *Applied Catalysis A: General* 384.1-2 (2010): 213-219.
- Goud, V.V., A.V. Patwardhan, and N.C. Pradhan. "Studies on the epoxidation of mahua oil (*Madhumica indica*) by hydrogen peroxide". *Bioresource technology*. 97.12(2006):1365-1371.
- Guidotti, M., N. Ravasio, R. Psaro, E. Gianotti, S. Coluccia, & Marchese, L. "Epoxidation of unsaturated FAMES obtained from vegetable source over Ti (IV)-grafted silica catalysts: A comparison between ordered and non-ordered mesoporous materials". *Journal of Molecular Catalysis A: Chemical*, 250.1-2(2006): 218-225.
- Öktemer, A., H. Kocabas, N. Kınayoglu, I. Demir. *Organik Kimya ve Uygulaması, Milli Eğitim Basımevi*, (2001).

- Rios, L. A. , P. Weckes, H. Schuster, and W. F. Hoelderich. "Mesoporous and amorphous Ti-silicas on the epoxidation of vegetable oils." *Journal of Catalysis* 232.1(2005): 19-26.
- Sales, H., R.Cesquini, S. Sato, D. Mandelli, & U. Schuchardt. "Epoxidation of soybean oil catalysed by $\text{CH}_3\text{ReO}_3/\text{H}_2\text{O}_2$ ". *Studies in Surface Science and Catalysis*. (2000).
- Santacesaria, E., R. Tesser, M. Di Serio, R. Turco, V. Russo, & D.Verde. " A biphasic model describing soybean oil epoxidation with H_2O_2 in a fed-batch reactor". *Chemical Engineering Journal* 173.1(2011): 198-209.
- Saremi, K., T. Tabarsa, A. SHakeri, & A. Babanalbandi. "Epoxidation of soybean oil". *Annals of biological research* 3.9(2012): 4254-4258.
- Serio, M. D.,R. Turco, P. Pernice, A. Aronne, F. Sannino, & E. Santacesaria. "Valuation of $\text{Nb}_2\text{O}_5\text{-SiO}_2$ catalysts in soybean oil epoxidation". *Catalysis Today* 192.1(2012):112-116.
- Sienkiewicz, A. M., P. Czub."The unique activity of catalyst in the epoxidation of soybean oil and following reaction of epoxidized product with bisphenol A". *Industrial Crops and Products* 83(2016):755-773.
- Sharma, R. V., K.K. Soni, & A.K. Dalai. "Preparation, characterization and application of sulfated Ti-SBA-15 catalyst for oxidation of benzyl alcohol to benzaldehyde". *Catalysis Communications* 29(2012): 87-91.
- Sharma, R. V., Baroi, C., & Dalai, A. K. Production of biodiesel from unrefined canola oil using mesoporous sulfated Ti-SBA-15 catalyst. *Catalysis Today*, 237, (2014): 3-12.
- Zhang, H., H. Yang, H. Guo, J. Yang, L. Xiong, C. Huang, X. Chen, L. Ma, and Y. Chen. "Solvent-free selective epoxidation of soybean oil catalyzed by peroxophosphotungstate supported on palygorskite". *Applied Clay Science*, 90(2014):175-180.

APPENDIX A

NMR SPECTRA OF EPOXIDIZED SOYBEAN OIL WITH SYNTHESIZED CATALYSTS FOR OTHER REACTION TIME

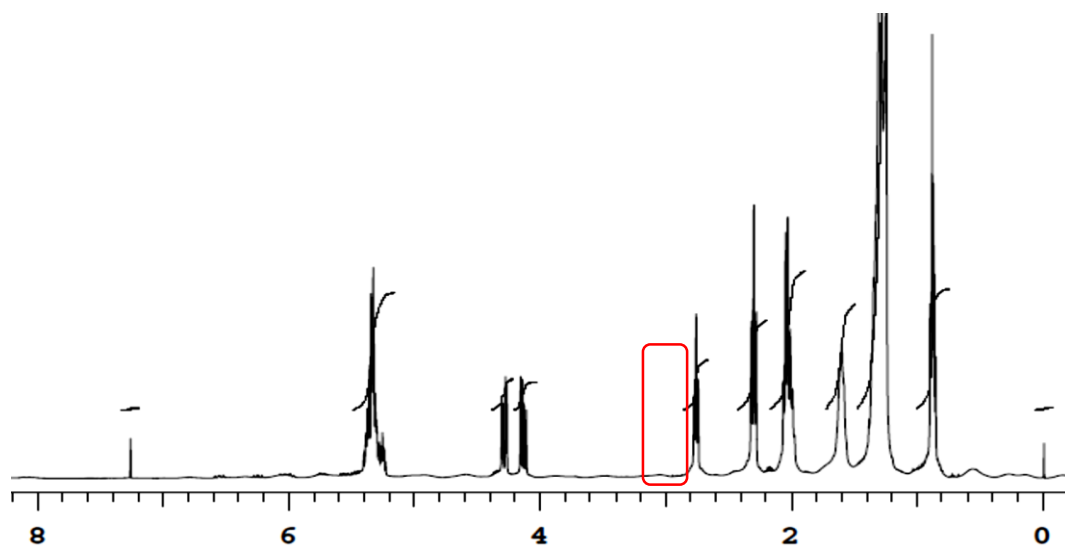


Figure A.1. ¹H-NMR spectra of epoxidized soybean oil with TSB10 for 2h of reaction time.

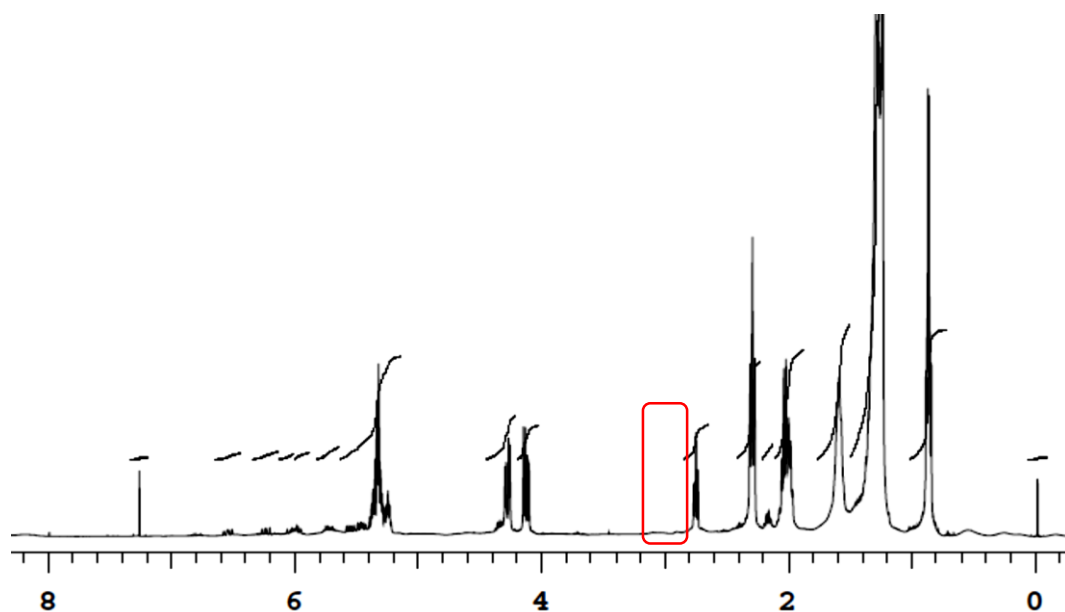


Figure A.2. ¹H-NMR spectra of epoxidized soybean oil with TSB10 for 4h of reaction time.

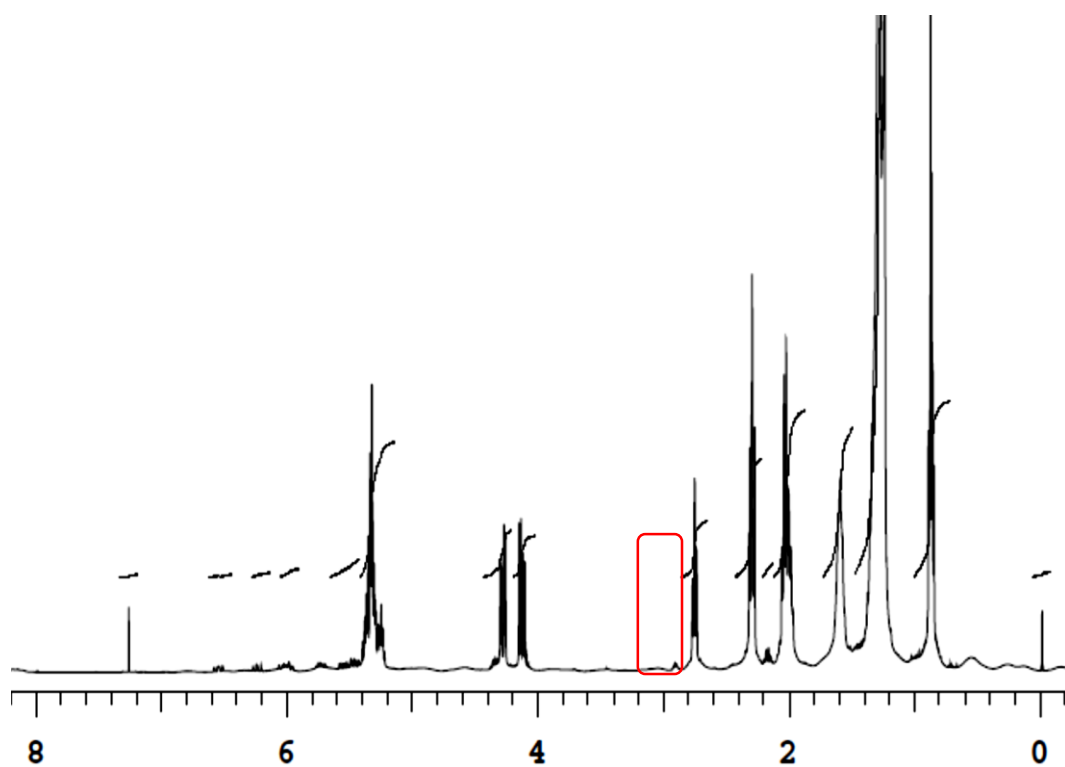


Figure A.3. H-NMR spectra of epoxidized soybean oil with 8MTSB10 for 2h of reaction time.

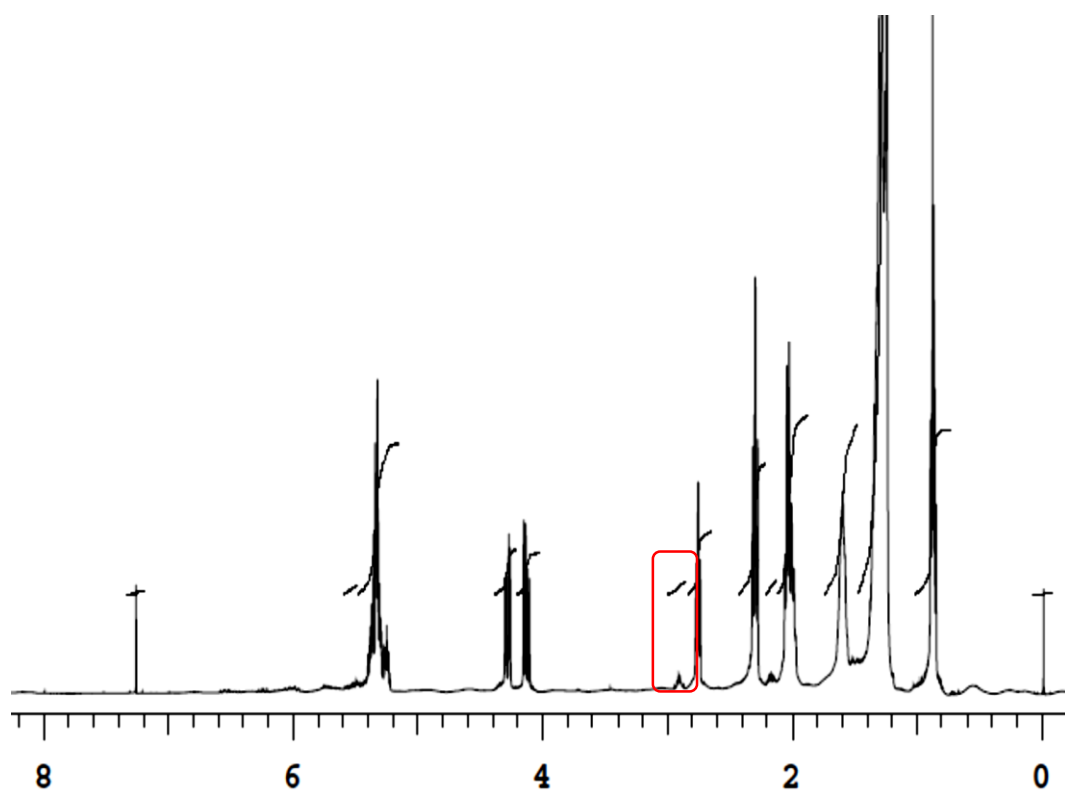


Figure A.4. H-NMR spectra of epoxidized soybean oil with 8MTSB10 for 4h of reaction time.

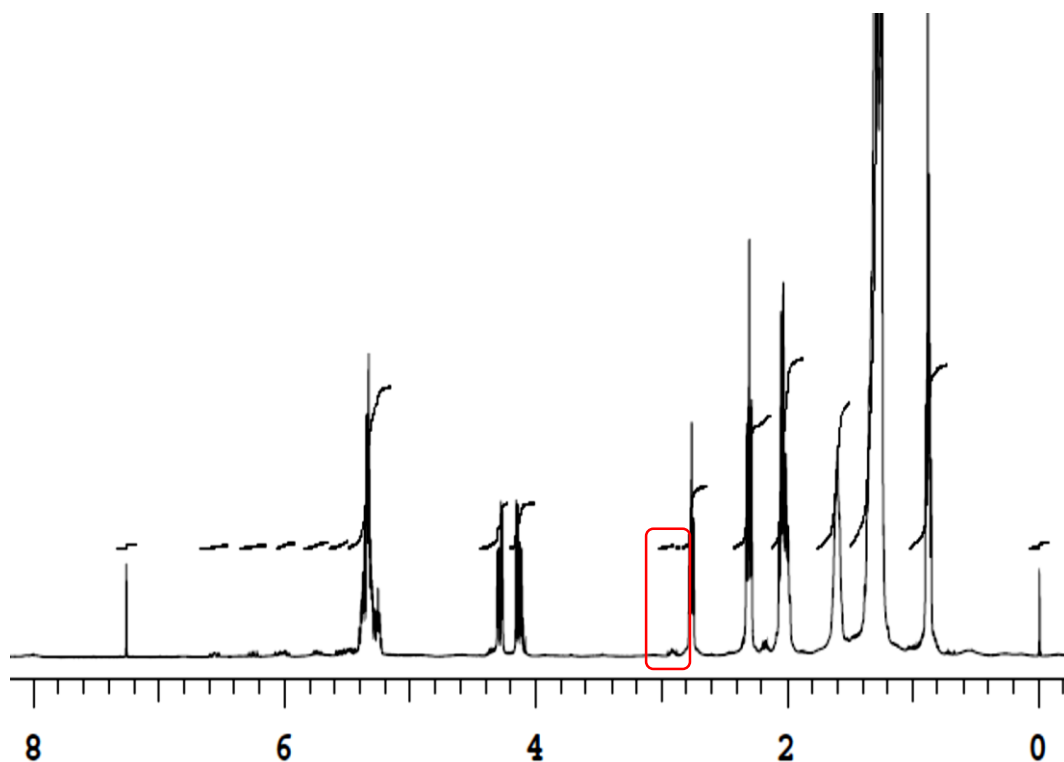


Figure A.5. ¹H-NMR spectra of epoxidized soybean oil with 12MTSB10 for 2h of reaction time.

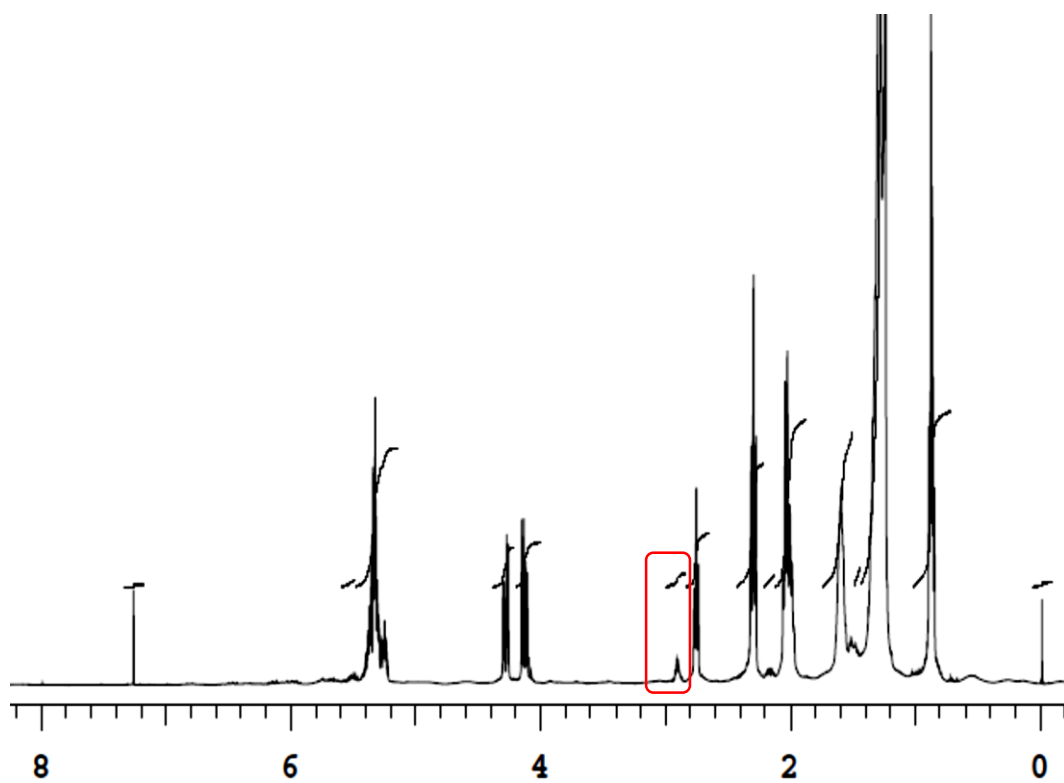


Figure A.6. ¹H-NMR spectra of epoxidized soybean oil with 12MTSB10 for 4h of reaction time.

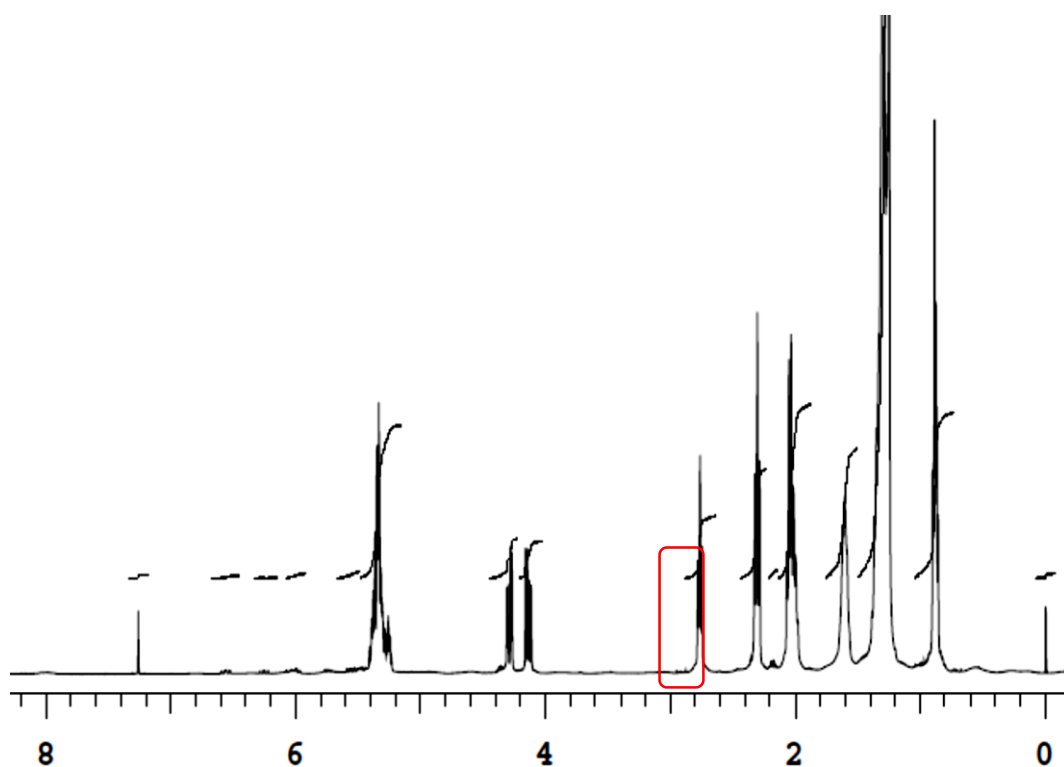


Figure A.7. ¹H-NMR spectra of epoxidized soybean oil with TSB20 for 2h of reaction time.

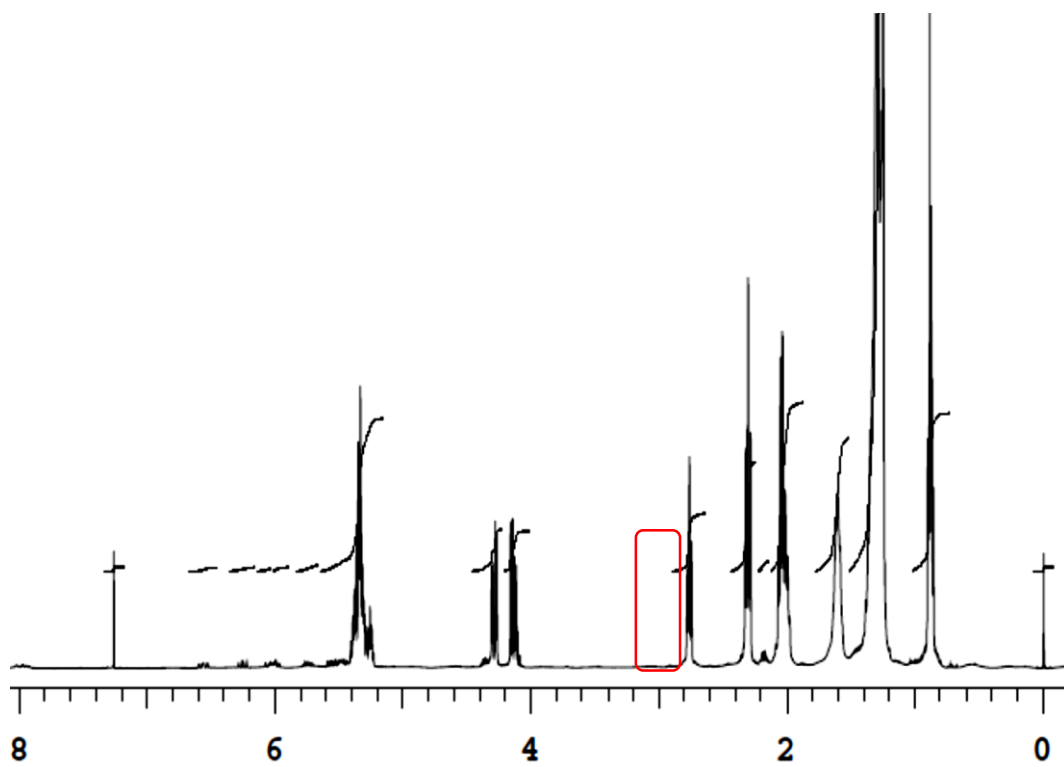


Figure A.8. ¹H-NMR spectra of epoxidized soybean oil with TSB20 for 4h of reaction time.

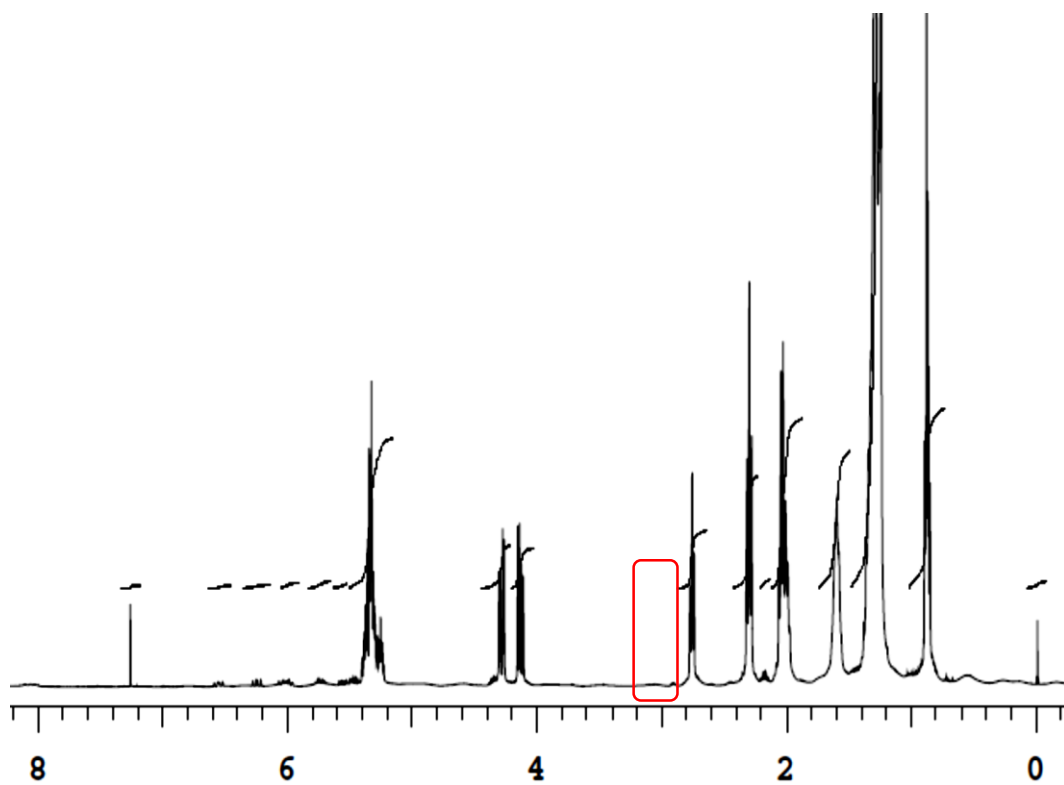


Figure A.9. ¹H-NMR spectra of epoxidized soybean oil with 8MTSB20 for 2h of reaction time.

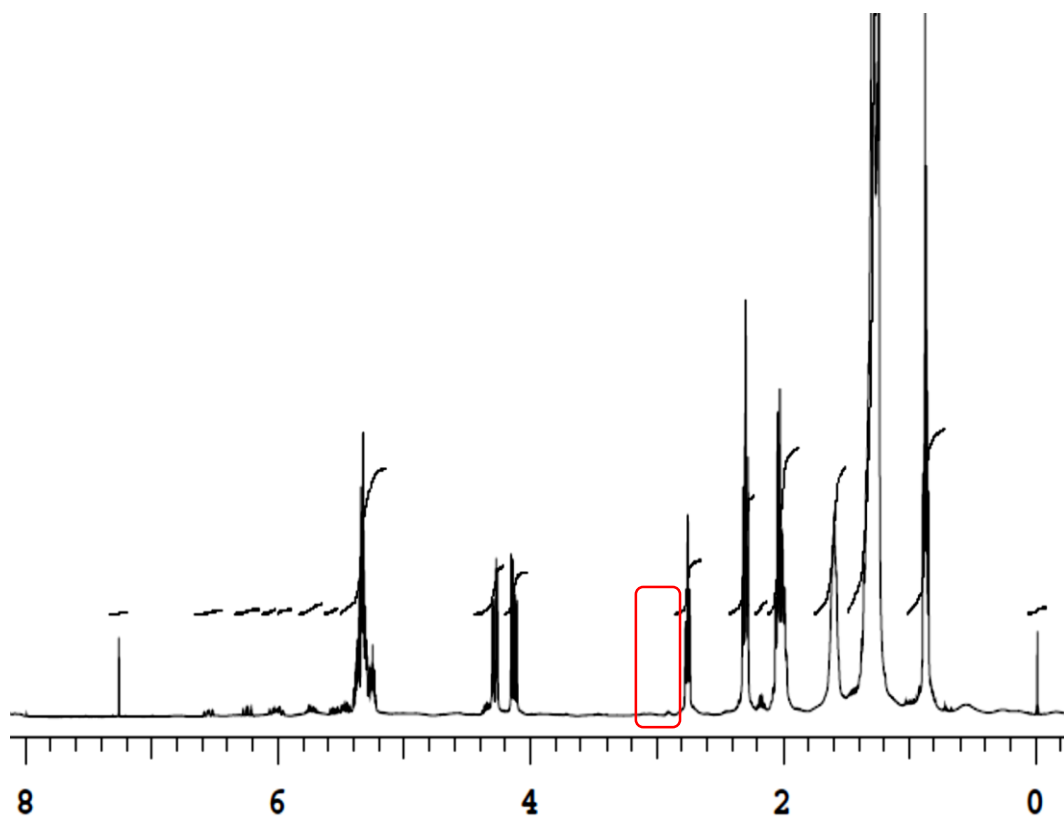


Figure A.10. ¹H-NMR spectra of epoxidized soybean oil with 8MTSB20 for 4h of reaction time.

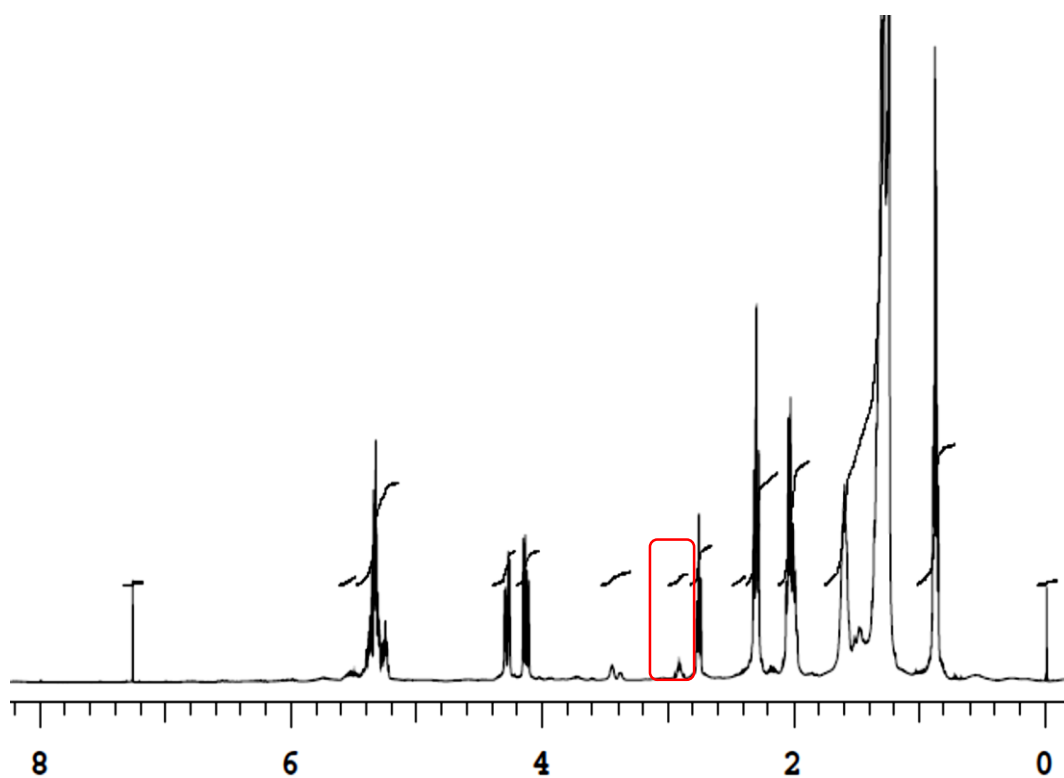


Figure A.11. ¹H-NMR spectra of epoxidized soybean oil with 12MTSB20 for 2h of reaction time.

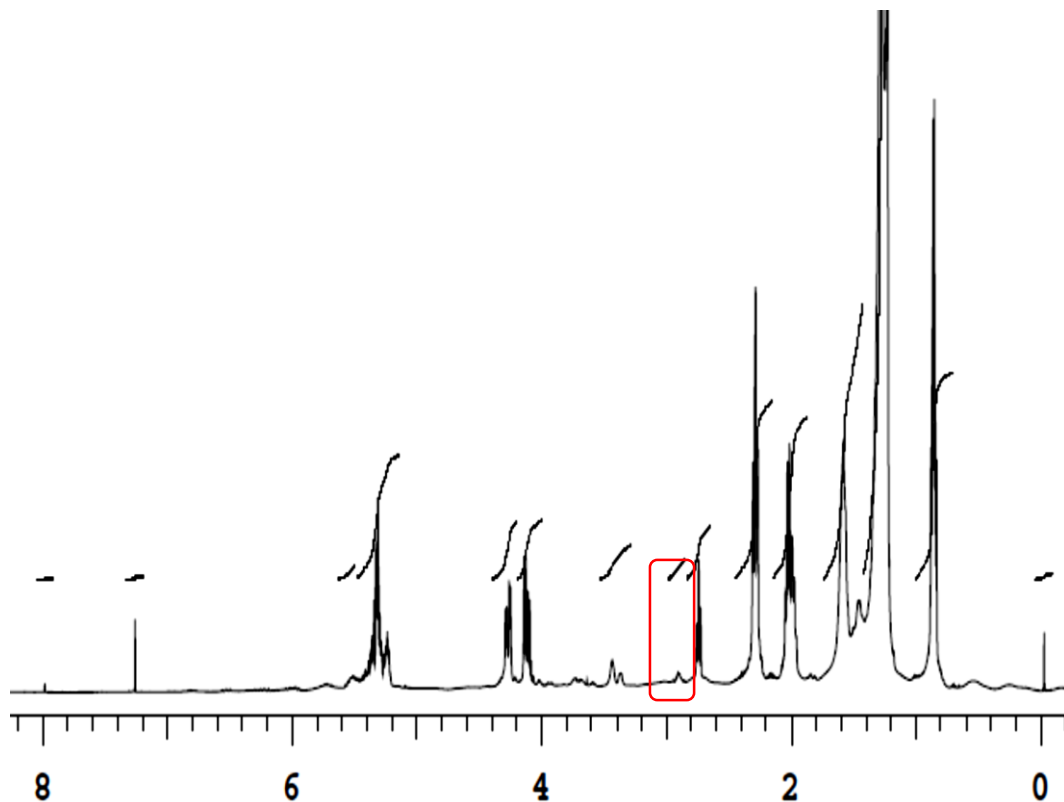


Figure A.12. ¹H-NMR spectra of epoxidized soybean oil with 12MTSB20 for 4h of reaction time.