ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

PREPARATION OF POROUS POLYMERS BY EMULSION TEMPLATE METHOD AND THEIR USE IN BIODIESEL PRODUCTION

M.Sc. THESIS

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Department of Polymer Science and Technology

Polymer Science and Technology Programme

JANUARY 2024

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

EMÜLSİYON ŞABLON YÖNTEMİYLE GÖZENEKLİ POLİMERLERİN HAZIRLANMASI VE BİYODİZEL ÜRETİMİNDE KULLANILMALARI

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Büşra Ay Tuncer, a M.Sc. student of ITU Graduate School, student ID 515201002, successfully defended the thesis entitled "PREPARATION OF POROUS POLYMERS BY EMULSION TEMPLATE METHOD AND THEIR USE IN BIODIESEL PRODUCTION", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my beloved mother,

FOREWORD

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ABBREVIATIONS

BAS : Brønsted acid sites
BCC : Body centered cubic
BET : Brunauer–Emmett–Teller
BJH : Barrett−Joyner−Halenda
CMC : Critical Micelle concentration
DCE : Dichloroethylene
DVB : Divinylbenzene
FCC : Face Centered Cubic
FFA : Free Fatty Acid
FT-IR : Fourier Transform Infrared Spectroscopy
GMA : Glycidyl Methacrylate
HIPE : High Internal Phase Emulsion
HMF : Hydroxymethylfurfural
HXL-PHP : Hypercrosslinked Polyhipe
IPA : Isopropyl Alcohol
MB : Methylene Blue
MOF : Metal Organic Framework
MSN : Mesporous Silica Nanporticles
PEI : Polyethylenimine
PGA : Polyglutaraldehyde
PTFE : Polytetrafluoroethylene
SC : Simple Cubic
SEM : Scanning Electron Microscope
SET : Simultaneous Esterification and Transesterification
STY : Stryene
TOF : Cycle Frequency
TON : Number of Cycles
UV : Ultraviolet
VBC : Vinylbenzyl Chloride
WCO : Waste Cooking Oil

SYMBOLS

<D>	**:** Pore diameter
<d>	**:** Window diameter
<d>/<D>	**:** The degree of interconnections
µg	**:** Microgram
µm	**:** Micron
g	**:** Gram
h	**:** Hour
L	**:** Liter
m	**:** Mass
M	**:** Molarity
mg	**:** Milligram
min	**:** Minute
mL	**:** Milliliter
mmol	**:** Millimol
nm	**:** Nanometer
^{o}C	**:** Degree Celcius
rpm	**:** Round per minute
S_{BET}	**:** BET surface area
T	**:** Temperature
v	**:** Volume
v_p	**:** Pore volume
w	**:** Weight

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PREPARATION OF POROUS POLYMERS BY EMULSION TEMPLATE METHOD AND THEIR USE IN BIODIESEL PRODUCTION

SUMMARY

High Internal Phase Emulsions were prepared to obtain highly porous polymers as solid catalysts for esterification of oleic acid with methanol. High internal phase emulsion method enables preparing porous polymers with interconnectivity. However, the surface area of these polymers is extremely constrained as a result of very large pores. This drawback was overcome through hypercrosslinking reaction. PolyHIPEs were prepared using VBC as a monomer and DVB as a crosslinker, followed by a hypercrosslinking process to produce high-surface-area polymers. The hypercrosslinking reaction was applied through Friedel-Crafts alkylation reaction catalyzed by a Lewis acid $FeCl_3$ where chloromethyl group acts as an internal electrophile, and DCE as solvent and external crosslinker. Because DCE has a boiling point of 80°C, it enables the reaction to take place at high temperatures while simultaneously acting as an external crosslinker for the hypercrosslinking process. This reaction produces micro/meso pores and high specific surface area within the framework of polyHIPE precursor. The hypercrosslinking reaction is a controlled reaction that allows an increase of the surface area in a controlled way leaving some unreacted pendant groups. The unreacted pendant groups were employed for additional functionalization on the polymer surface, resulting in acid groups. The catalytic acitivity of the functional unhypercrosslinked and hypercrosslinked solid catalysts were validated through the esterification of oleic acid with methanol for biodiesel production. In addition, this study showed that it is possible to control the amount of sulfonic acid groups and the hydrophobicity of the polymer surface by attaching the sulfonic acid groups in PolyHIPE to the polymer via a methylene bridge. The morpholgy of the polymer surfaces were charactrized by SEM and BET surface area measurements were used to determine the surface area, pore size, and pore size distributions. The surface functionality was characterized by FT-IR and acid-base titration. The good yields were obtained for the esterification reaction with 10% of the solid catalyst at 90^{o}C. Furthermore, the application of the hypercrosslinked solid acid catalyst resulted in enhanced reaction kinetics when compared to the unhypercrosslinked equivalent. The high-surface-area solid acid catalysts can be reused at least four times with relatively negligible activity loss.

EMÜLSİYON ŞABLON YÖNTEMİYLE GÖZENEKLİ POLİMERLERİN HAZIRLANMASI VE BİYODİZEL ÜRETİMİNDE KULLANILMALARI

ÖZET

Sürdürülebilirlik günümüz dünyasında önemli bir konu haline gelmiştir. Özellikle enerji alanında yenilenebilir kaynaklar değerlendirilmelidir. Bu kapsamda yenilenebilir bir kaynak olan, karbon ayak izi düşük, sürdürülebilir, ayarlanabilir fiziksel ve kimyasal özelliklere sahip olan biyodizel dizele aternatif olarak değerlendirilmiştir. Biyodizel üretiminde en yaygın süreç transesterifikasyon-esterifikasyondur. Transesterifikasyon reaksiyonunda yüksek sıcaklık, yüksek basınç ve reaksiyon süresini minimalize edebilmek için katalizör kullanılması tercih edilir. Katalizörler, bir kimyasal reaksiyonun aktivasyon enerjisini azaltan, termodinamiğini etkilemeden reaksiyonu hızlandıran ve reaksiyonun sonunda değişmeden kalan malzemelerdir. Bu çalışma için serbest yağ asitlerinin esterifikasyonunu katalize ederken aynı zamanda trigliseritlerin transesterifikasyonunu da katalize edebilen heterojen asit katalizörleri kullanılmıştır. Ve bu katalizör emülsiyon şablonlama yöntemi kullanılarak elde edilmiştir. Emülsiyon şablonlama metodu ile iç faz oranı 0,74'e ulaştığında yüksek konsantrasyonlu, yüksek gözenekli Yüksek iç faz emülsiyonları oluşur. Bu oran 0,99'a kadar çıkabilir. Yüksek İç Faz Emülsiyonları, oleik asidin metanol ile esterleştirilmesinde katı katalizör olarak yüksek gözenekli polimerler elde etmek için hazırlanmıştır. HIPE'ler ayarlanabilir faz hacmine sahip oldukça gözenekli malzemelerdir. HIPE malzemeleri üretmek için iç faz yavaş yavaş dış faza eklenir. Ayrıca bu işlem, yüksek hızda karıştırırken büyük damlacıkları daha küçük damlacıklara ayırır. HIPE malzemesi elde edildikten sonra, sürekli fazın iç faz damlacıklarının çevresinde sertleşebilmesi (sürekli bir film oluşturabilmesi) için bir kalıba aktarılır. Burada sıcaklık parametresi ile polimer filmin en ince noktalarında kırılmalar meydana gelir ve iç faz damlacıkları uzaklaştırılarak sürekli gözenekler arasında birbirine oldukça bağlı hiyerarşik gözenek yapısına sahip açık hücreli köpüklü polimerik malzemeler oluşturulur. Bu polimere polyHIPE adı verilir. PolyHIPE malzemelerinin hazırlanmasında monomer olarak vinilbenzil klorür ve çapraz bağlayıcı olarak DVB kullanılmıştır. PolyHIPE'ların yüzey alanı, çok büyük gözeneklerin bir sonucu olarak son derece kısıtlıdır. Yüzey alanı, DVB gibi çapraz bağlama maddeleri kullanılarak bir hiper çapraz bağlama işlemi gerçekleştirilerek artırılmıştır. Hiper çapraz bağlama reaksiyonu, klorometil grubunun bir iç elektrofil olarak hareket ettiği bir Lewis aside, $FeCl_3$, tarafından kataliz edilen Friedel-Crafts alkilasyon reaksiyonu ve hem çözücü hem de dış çapraz bağlayıcı olarak DCE aracılığıyla 15 dk uygulanmıştır. DCE 80°C kaynama noktasına sahip olduğundan, reaksiyonun yüksek sıcaklıklarda gerçekleşmesini sağlarken aynı zamanda hiper çapraz bağlama işlemi için harici bir çapraz bağlayıcı görevi görür. Bu reaksiyon, poliHIPE öncüsü çerçevesinde mikro/mezo gözenekler ve yüksek spesifik yüzey alanlı HXL-15min-PHP katalizörünü üretir. Katalizörün gözenekli yapısı önemlidir. Gözenekli yapılar sayesinde kütle aktarımı yüzeyin yanı sıra reaktif alanlarda da gerçekleşebilir. Sonuç olarak, mikro gözenekliliğin yanı sıra mezo/makro gözeneklere sahip hiyerarşik gözenekli katalizörlerin oluşturulması, katalitik performansı ve

difüzyon özelliklerini geliştirir. Hiper çapraz bağlama reaksiyonu, yüzey alanının kontrollü bir şekilde artmasını sağlayan ve bazı reaksiyona girmemiş pendant grupları bırakan kontrollü bir reaksiyondur. Reaksiyona girmemiş pendant gruplar polimer yüzeyinde ilave fonksiyonelleştirme için kullanılmış ve asit grupları elde edilmiştir. Bu çalışmada hem polyHIPE malzemesin hem de yüksek çarpraz bağlı HXL-15min-PHP malzemesinin yapısına sülfonik asit grubu eklemek için belli modifikasyon adımları gerçekleşmiştir. Bu adımlar sonucunda metilen köprüsü aracılığıyla polyHIPE malzemelere sülfonik asit grubu eklenmiştir. PoliHIPE'deki sülfonik asit gruplarının bir metilen köprüsü aracılığıyla polimere bağlanması ile sülfonik asit gruplarının miktarının ve polimer yüzeyinin hidrofobikliğini kontrol etmenin mümkün olabileceği görülmüştür. Doğrudan sülfonik asit grubu bağlı PolyHIPE malzemesi ile sülfonik asitin metilen köprüsü aracılığıyla bağlı olduğu polyHIPE malzemesinin yeniden kullanılabilirliğini kanıtlamak için, esterifikasyon işlemi sonrasında vakum altında süzülerek ve ardından aktif bölgeleri yeniden oluşturmak için fazla metanol ile yıkanarak reaksiyon ortamından izole edildi. Ardından her iki katalizörün verimliliği birden fazla katalitik döngüde karşılaştırıldı. Yapılan denemeler sonucunda kontrollü bir şekilde elde edilen sülfonik asit gruplarına sahip poliHIPE katalizörlerinin, doğrudan sülfonasyonla elde edilene kıyasla daha iyi stabiliteye ve geri dönüştürülebilirliğe sahip olduğu görüldü. Ek olarak katalizörlerin yüzey morfolojik yapıları SEM ile analiz edildi. Yapılan yüksek çarpraz bağlama işleminin ve fonksiyonkaştırma adımlarının yüzey morfolojik yapısında çok ciddi değişikliklere neden olmadığı tespit edildi. PolyHIPE ve HXL-15min-PHP malzemesinin yüzey alanı ve hiper çapraz bağlanma reaksiyonunun gözenek boyutu ve gözenek boyutu dağılımı üzerindeki etkisi BET analizi ile incelendi. Bet analizi sonucunda PolyHIPE'nin yüzey alanı 10,46 m^2/g iken HXL-15min-PHP ‘in yüzey alanı 257,1 m^2/g olarak bulunmuştur. Ek olarak hiper çapraz bağlanma reaksiyonuyla gözenek hacminin sadece 15 dakikada 10 kattan fazla arttığı tespit edilmiştir. FTIR ile her bir modifikasyon adımı incelenmiş ve yapıya eklenen fonksiyonel grupların nitel analizi yapılmıştır. PolyHIPE ve yüksek çarpraz bağlı polyHIPE malzemesinin yapısındaki Cl^- içeriğini belirlemek önemlidir ve bu analiz cıva(II) tiyosinat yöntemiyle UV spektrumunda yapılmıştır. Klor tayinine dayalı hesaplamalara göre VBC polyHIPE öncüsü 5,8 mmol/g klor içeriğine, HXL-15min-PHP ise 3,4 mmol/g klor içeriğine sahiptir. Bu sonuçlar, yüksek dönüşümleri kanıtlayan sülfonik asit içeriği belirleme sonuçlarıyla iyi bir uyum içindedir. Bu çalışmada kataliz deneylerini gerçekleştirmek için iki temel amaç vardır: Birincisi, metanol ve oleik asit arasındaki esterleşme reaksiyonu için yüksek katalizör verimi ve geliştirilmiş reaksiyon kinetiği ve ikincisi, metilen köprülü poliHIPE katalizörünün avantajının kanıtlanması. Katalizörün aktivitesi, esterleşme reaksiyonu sırasında asit değerinin azalmasıyla belirlendi. Bu çalışmada asıl amaç biyodizel üretiminde atık yağların değerlendirilebilmesini sağlamaktır. Atık yağlardaki serbest yağ asitlerinin yüksek içeriği nedeniyle bu yağların doğrudan kullanımı toksik olabilir ve biyodizel üretmek için transesterifikasyon için kullanılan temel katalizörleri devre dışı bırakabilir. Bu nedenle, atık yağlardaki serbest yağ asit değerini azaltmak amacıyla ön işlem olarak asit katalizörleri tarafından katalize edilen esterifikasyon gereklidir. Bu tezde hazırlanan gözenekli polimerler, daha verimli bir biyodizel üretimi için bu ön arıtma işleminde kullanılabilir. Katalitik verimlilik kullanılan katalizör miktarı, metanol/oleik asit oranı, reaksiyon sıcaklığından etkilenir. Bu nedenle bu çalışmada ilk olarak bu parametreler belirlendi. Bu çalışmada %10 oranında bir dereceye kadar hidrofobikliğe sahip, ait heterojen baz katalizörleri kullanıldı. Sonuç olarak mol sayısına bağlı olarak %10 mol katalizör miktarı ile %77,5 oranında oleik asit elde edilebilmiştir. Katalizör

miktarındaki daha fazla artış katalitik performansı değiştirmediğinden sonraki katalitik deneylerde %10 uygulandı. Oleik asit ile metanol arasındaki reaksiyon geri dönüşümlü olduğundan bu oran çok önemlidir ve ileri reaksiyonu arttırmak için metanolün oleik asit molar oranının teorik değer olan 1'den büyük olması gerekir. Oranı 3'ten 8'e çıktıkça 90^{o}C'de esterleşme verimi %42,14'ten %68,37'ye çıktı. Ayrıca oran 8'den fazla kırılma reaksiyonunun aynı değerde kaldığı gözlendi. Reaksiyon sıcaklığı 25°C'den 100°C'ye çıktıkça verim %32,2'den %76,5'e çıkmıştır. Çünkü esterleşme reaksiyonu endotermik bir reaksiyondur. Ek olarak nedenle PolyhIPE ve HXL-15min-PHP'in katalitik aktivitesi aynı esterifikasyon koşulları altında karşılaştırıldı. HXL-15min-PHP'e bağlı sülfonik asit grupları, polyHIPE'ye kıyasla reaksiyon kinetiğini arttırmıştır. Ayrıca mezo ve mikro gözeneklerin elde ettiği yüksek yüzey alanı reaktanların yüzey aktif gruplara daha hızlı ulaşmasını sağlayarak daha kısa sürede yüksek verim sağlamıştır.

1. INTRODUCTION

The planet in which we live is becoming increasingly polluted and going extinct as a consequence of the population growth and the subsequent rise in consumption. The increasing rate of consumption must be harmonized with the increasing number of people. The scarce resources utilized make this situation problematic. The adverse effects that are obvious increase gradually as difficulties arise. In this context, sustainability is now recognized as a significant global concern. There has been a trend toward clean, reliable, and renewable alternative sources appropriate for a circular economy, particularly in the energy industry. Since fossil resources are non-renewable resources that are exhausted and severely damage the environment when they are converted into products. Currently, biofuels as alternative energy sources, particularly biodiesels, which are biodegradable, non-toxic, and have several advantages over fossil fuels, have a very broad and special utilization industries [1]. Biodiesel can be obtained by many methods. Biodiesel obtained using catalysts is more efficient, durable and sustainable. Catalysts are porous materials with a certain chemical structure and surface area that affect the activity in the reaction. Catalysts can be obtained by high internal phase emulsion (HIPE) method. The surface area of the catalyst obtained by this method is limited. HIPEs are concentrated systems with a hierarchical pore structure and a dispersed phase with a volume fraction above 74% [2]. The polymeric material obtained by this method is identified as polyHIPE material.

In this study, as solid catalysts for the esterification of oleic acid with methanol, it aims to prepare HIPEs to obtain highly porous polymers and the functionalization to increase catalytic activity. In addition, it aims to obtain polymers with high surface area by hyper cross-linking reaction and a suitable hydrophobicity through the controlled functionalization.

2. THEORETICAL PART

2.1 Biodiesel

One of these alternative energy sources is biodiesel, which is a renewable resource, has a low carbon footprint, is sustainable, and has tunable physical and chemical characteristics [3]. Using diesel in the form of biodiesel, which has a wide range of applications, is a progress that also contributes to the circular economy.

After consumption, petroleum-based diesels create pollutants such as high quantities of CO_2, SO_2, and soot, causing environmental contamination. These pollutants damage nature in the long term. At this point, using biodiesel has a significant benefit. Biodiesel releases less pollutants than petroleum-based diesel [4].

Biodiesel is a non-toxic, sulfur-free, and biodegradable monoalkyl ester that can be produced from waste oils, microalgae, animal fats, and vegetable oils [5]. Aside from all of these benefits, there is one challenge that biodiesel manufacturing must overcome: making biodiesel production profitable. As an alternative to traditional biodiesel manufacturing, using more technologically sophisticated, advanced, and sustainable catalysts is a step that may increase profitability and efficiency.

The selection of raw materials used in biodiesel synthesis is critical since it impacts free fatty acid (FFA). FFA are free fatty acids that are not bound to triglycerides. As the FFA ratio increases, the rate of soup formation increases, which reduces the catalytic efficiency of the catalyst in biodiesel production and increases the viscosity of the biodiesel and negatively affects the purification process [6]. The FFA ratio varies based on the kind of fat. FFA content of animal fats exceed 20%, vegetable oils are around 1.5%, and edible oils are less than 4% [5-6] Oils containing less than 2.5% FFA are suitable for biodiesel production. Raw material used above this value may cause an increase in cost as pre-treatment is required. Otherwise, the transesterification process becomes difficult. With the right choice of raw material, the right technique, and the appropriate catalyst, the process can be facilitated, and high-efficiency biodiesel can be obtained.

There are four different standard techniques for biodiesel production [5]. These are:

i. Direct use blended oils: In this technique, the raw material (oil) is diluted with petroleum diesel. This reduces the viscosity and makes it suitable for biodiesel production.

ii. Microemulsion of oils: The raw material is mixed with appropriate solvents such as methanol, ethanol, and amphiphilic compounds (such as surfactants) in this process.

iii. Thermal cracking (pyrolysis) of oils: With this technique, large molecule compounds are thermally broken down into smaller molecules in the absence of air and oxygen.

iv. Transesterification: The most common process for producing biodiesel is transesterification. Transesterification is an equilibrium reaction, as can be seen in equations (2.1)-(2.3), it consists of a series of reversible processes.

$$\text{Triglyceride} + R^1\,OH \rightleftharpoons \text{Diglycerdie} + RCOOR^1 \quad (2.1)$$

$$\text{Diglyceride} + R^1\,OH \rightleftharpoons \text{Monoglycerdie} + RCOOR^1 \quad (2.2)$$

$$\text{Monoglyceride} + R^1\,OH \rightleftharpoons \text{Glycerol} + RCOOR^1 \quad (2.3)$$

Triglycerides are converted to diglycerides in the first step, then to monoglycerides and glycerol in the second, and a methyl ester molecule is produced in each step [7]. This is an efficient approach for reducing viscosity. Oils and alcohols are esterified in the presence of a catalyst in this process. As a result of this process, biodiesel and glycerin are produced as byproducts. Excess alcohol is collected and recycled back to the first step after these two products have been separated. This method is more environmentally friendly than others. The transesterification reaction occurs in the absence of a catalyst as well, however it requires a high process temperature, high pressure, and a long period of time to proceed, thereby raising the cost [1]. The presence of a catalyst is therefore desired for all of these processes. Determining an appropriate catalyst is crucial.

2.2 Catalysts

Catalysts are materials that reduce the activation energy of a chemical reactions, accelerate the reaction without influencing its thermodynamics, and remain unchanged at the end of the reaction [8]. Aspects such as selectivity, activity, and stability are useful for evaluating a catalyst's performance. In catalytic systems, activity is defined as the rate at which reactants are converted into products. Activity is influenced by the catalyst's surface area and chemical composition. The capacity to catalyze a favored reaction in a chemical reaction is recognized as selectivity. More than one reaction (side reaction) may take place simultaneously in a chemical reaction. In this context, the catalyst's selectivity plays a significant role in efficiency. Thus, side reactions can also be managed. Stability is a concept that describes how long a catalyst remains active. In general, all three of these concepts should be taken into consideration dependently in order to obtain an effective catalyst.

The concepts of TON (number of cycles) and TOF (cycle frequency) can assist researchers comprehend a catalyst's efficiency. TOF is a measure of a catalyst's instantaneous efficiency. It refers to the TON per unit of time. The total number of substrate molecules converted by a catalyst into product molecules is known as the TON, which is the highest product yield that can be achieved from the catalytic center [9-10].

Catalysts of different kinds are employed in the production of biodiesel. The catalysts used in biodiesel manufacturing are classified in this section. The catalysts used in the production of biodiesel are listed in Figure 2.1 [11].

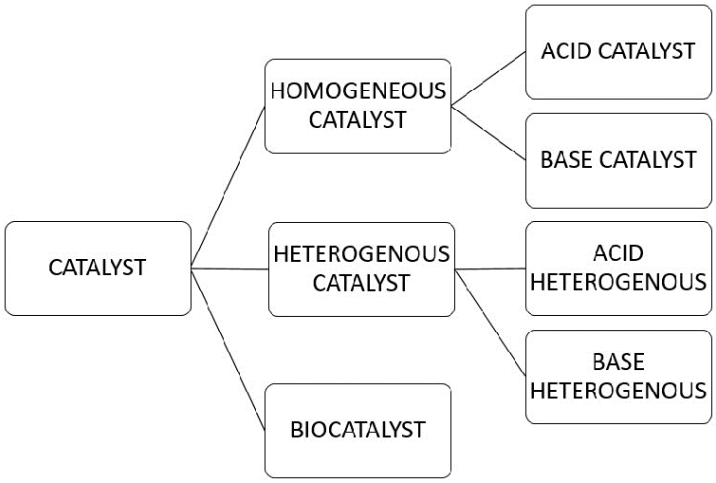

Figure 2.1 : Catalyst used in biodiesel production technology.

As shown in Figure 2.1, catalysts used for biodiesel synthesis are classified into two categories: homogeneous and heterogeneous. There are acid and basic catalysts in both categories.

2.2.1 Homogenous catalysts

The term "homogeneous catalyst" refers to a catalyst that is in the same phase as the reaction phase. Although homogeneous catalysts have advantages such as the ability to produce high efficiency biodiesel under ideal conditions and the ability to produce biodiesel at low temperatures, their use in industrial applications is constrained by their drawbacks, particularly the complicated recycling process and high operating costs [12].

2.2.2 Heterogeneous catalysts

A heterogeneous catalyst is one that is in a different phase than the reaction phase. Heterogeneous catalysts are also classified according to the sites they possess [13]. These are;

i. Heterogeneous acid catalyst
ii. Heterogeneous base catalyst
iii. Heterogeneous acid-base catalyst

The transesterification reaction using a heterogeneous catalyst for biodiesel production is described by the Eley-Rideal mechanism [14]. To explain in three steps, first of all, all three of these catalysts react with an alcohol, such as methanol, as in homogeneous catalysts, to form an alcoholite group. As a result, the alcohol is adsorbed onto the catalyst. Then a surface reaction takes place with the reactant (oil) and the alcohol adsorbed on the catalyst. Finally, desorption of the glycerol formed takes place over the catalyst.

Heterogeneous acid catalysts are preferred over heterogeneous base catalysts because they can catalyze the esterification of FFAs while simultaneously catalyzing the transesterification of triglycerides [15].

Heterogeneous catalysts are preferable over homogeneous-based catalysts in industrial applications since they can be separated easily, are reused several times, are environmentally friendly in this application, and have reduced operating costs [3].

Heterogeneous catalysts are more ecologically harmless while homogeneous catalysts have corrosive characteristics [11].

In addition to all of these advantages, the effective surface area of heterogeneous acid-base catalysts is low [12]. This drawback can be overcome by increasing the active surface area. By modifying the pore size, pore density, and pore connectivity, it is possible to produce catalysts with adjustable morphology [16].

2.3 Porous Materials

The catalyst's porous structure is essential. Mass transfer can take place in reactive areas in addition to on the surface thanks to porous structures. Single microporous catalysts are useful in catalytic applications to enhance catalytic selectivity, but they may result in poor catalytic activity because they restrict the diffusion of reactants [17]. As a result, constructing hierarchical porous catalysts with meso/macro pores in addition to microporosity improves catalytic performance and diffusion characteristics. In one research, hierarchical porous catalysts of various sizes were produced by adjusting the internal phase ratio and the amount of surfactant used during catalyst synthesis, and it was found that porous catalysts of various sizes with interconnected and vacant voids performed more effective [18].

Porosity in a polymeric material can be achieved in a variety of methods. Figure 2.2 includes a list of these methods [19].

2.3.1 Colloidal templating

Colloid is a type of chemical mixture in which one of two substances is evenly dispersed in the other. There are two different phases. One is the dispersed phase (internal phase), and the other is the continuous phase. Particles of the substance in the dispersed phase remain suspended in the mixture. Therefore, they may have the appearance of a solution.

Colloidal systems usually have disordered and randomly compacted packing. The form of the droplets is spherical due to interfacial tension caused by molecular interactions between the two phases [20]. The spherical shape reduces pressure on the molecules within the droplet. The closest packing concentrations of these spherical

pathways for crystal structures such as simple cubic (SC), body-centered cubic (BCC), and face-centered cubic (FCC) are 0.524, 0.680, and 0.740 [20].

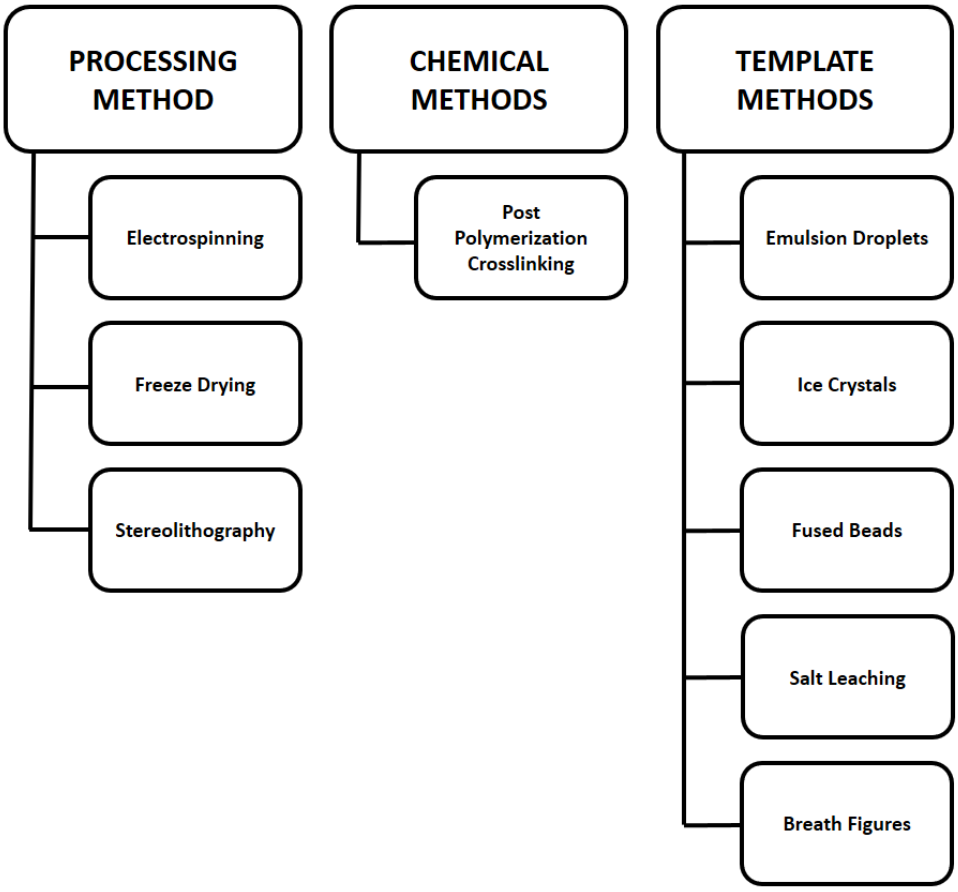

Figure 2.2 : Production methods for porous polymers.

Colloidal systems are techniques for producing porous materials [21]. The continuous phase is polymerized in these systems. The colloidal components are subsequently extracted from the system to produce a porous material. Among these colloidal systems are the following:

i. Emulsion droplets
ii. Bicontinuous microemulsion channels
iii. Water droplets
iv. Solid particles

The pore size and affected zone of the porous material vary depending on the colloidal system used.

2.3.2 Emulsion droplets template method

Emulsion templating is the most used method to prepare a porous material [19]. This method allows for the adjustment of the material's pore morphology and the production of materials with interconnected pore structures. The materials obtained using this method are also low-density, highly cross-linked materials.

Emulsion can be called the dispersion of one of two immiscible liquids in the form of droplets in the other liquid [22]. These liquids are usually water or oil. In emulsion polymerization, there are two phases: continuous phase, also known as the external phase, and dispersed phase, also known as the internal phase. It is named according to which phase the droplet forms. (like oil-in-water-in-oil and water-in-oil-in-water). In this method, monomers are first dissolved in the continuous phase, then monomer polymerization occurs, and finally the droplet phase is removed to obtain a porous polymer.

There is generally a water phase, oil phase, monomer, emulsifier (surfactant or emulsifying agent), and initiator for an emulsion polymerization to take place. First, micelles are formed from emulsifiers. Polymerization takes place in these micelles. Emulsifiers are also molecules that affect surface tension. Therefore, the surface tension decreases as micelle structures are formed. Following the formation of micelles, the surface tension eventually stabilizes and does not change. The critical micelle concentration (CMC) is the name given to this constant point. Emulsifiers are not aggregated and are free under the CMC. If the concentration of the surfactant in water decreases below this critical value, the inactivated micelles become unstable and disperse and dissolve in water. Therefore, in these emulsion systems, the CMC must be maintained in order for micelles to form and remain stable.

There are some factors which influence the emulsion droplet template method. These are the following parameters:

i. Reaction temperature
ii. Type and concentration of emulsifier
iii. Type and concentration of initiator
iv. Monomer
v. Mixing speed

The reaction temperature is a critical parameter in the emulsion droplet template method since it limits the effectiveness of emulsifiers. When the temperature increases, emulsifiers become insoluble in water and start to disperse in the oil phase. This causes the emulsion to break down and when the phase transformation temperature is reached, phase transformation starts [23]. Furthermore, initiators start to polymerize at a certain temperature range. In this regard, temperature is also critical for emulsion polymerization to take place [22].

Emulsifiers have a vital role in affecting emulsion particle size, lowering surface tension, and stabilizing the system. It does this by producing a film at the smallest contact of two immiscible liquids. Emulsifiers are made up of two parts: a hydrophilic head and a hydrophobic tail. In general, the hydrophilic part is oriented towards water and the hydrophobic part towards the oil phase. A balance is created in this way.

The monomer used in emulsion polymerization must also have a structure that can polymerize with free radicals, and the initiator used must be able to decompose at this temperature [22].

One of the physical characteristics influencing polymerization in emulsion polymerization is mixing speed. The rate of mixing should be maintained. If it is too fast, micelles may break up; if it is too slow, collapse may occur.

Emulsions are categorized into three types based on the particle size of the dispersed phase: microemulsions, macroemulsions, and nanoemulsions. Macroemulsions have particle sizes greater than 100 nm, microemulsions have particle sizes between 10 and 100 nm, and nanoemulsions have particle sizes less than 10 nm [24].

The properties of emulsions depend not only on which phase is used but also on the volume phase ratio and can be classified according to the volume phase ratio [22]. Based on low, medium, and high volume phase ratios, there are several classifications of emulsions. HIPEs are ones in which the internal phase volume is 74% larger than the emulsion volume. In this study, high-internal-phase emulsion-based materials were prepared.

2.4 High Internal Phase Emulsions (HIPEs)

Part of the spherical droplets within the emulsion system flatten to form a polyhedral shape and create inter-droplet layers. This layer is referred to as the plateau border

[20]**.** The inter-droplet interaction influences the plateau border since it encompasses the remaining portion of the continuous phase outside the inter-droplet layers. As the volume ratio increases, this border diminishes while the inter-droplet layer expands [20]. When the internal phase ratio reaches 0.74, highly concentrated, highly porous HIPEs are formed.

These materials are formed by deforming the droplet shape from a uniform sphere to a tetrahedron, exceeding the maximum packing fraction that is most efficient for regular monodisperse spheres [22, 25]**.** This ratio can be increased up to 99% [26]. Consequently, highly porous materials are produced with tunable phase volume. In HIPE formation, there are two phases, the inner phase and the outer phase. The inner phase is gradually added to the outer phase in the presence of surfactant in order to produce HIPE materials. Furthermore, this process breaks large droplets into smaller droplets while mixing at a high rate.

Thermodynamically unstable HIPEs exhibit different kinetic stability depending on the internal phase volume ratio, the type of monomer used, the type and volume of surfactant used. Each parameter in this case is a factor that influences the characteristics of the material produced by the HIPE method. For instance, excessively increasing the volume percentage of the internal phase results in Ostwald ripening, leading to the HIPE to collapse. The viscosity of HIPE changes depending on the surfactant's properties. If the viscosity increases excessively, it may result in a major problem as the mixing process and consequently the dispersion and partitioning of the droplets will be adversely affected and the pore morphology (pore diameter, surface area, etc.) will be affected. Therefore, each parameter is highly important.

2.5 Preparation of PolyHIPEs from HIPEs

PolyHIPEs are polymeric porous materials obtained by polymerization of HIPEs [22]. After the HIPE material is obtained, it is transferred to a mold so that the continuous phase can cure (form a continuous film) around the inner phase droplets. Here, with the temperature parameter, fractures occur at the thinnest points of the polymer film and the internal phase droplets are removed to form open-cell foamy polymeric materials with a highly interconnected hierarchical pore structure between continuous pores. This polymer is called polyHIPE. A typical polyHIPE structure is shown in Figure 2.3 [27].

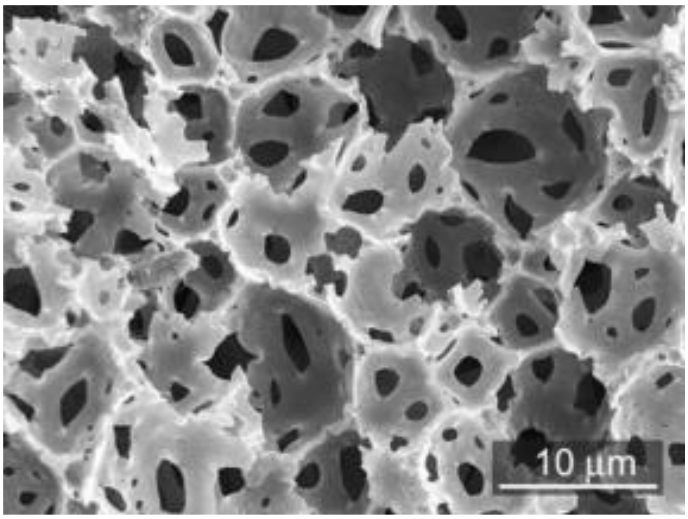

Figure 2.3 : A typical polyHIPE structure.

As shown in Figure 2.3, a PolyHIPE material consists of pores, also called voids, occupied initially by emulsion droplets and holes between neighboring pores, called windows or pore throats [20].

In the production of a PolyHIPE material, the internal phase (droplet phase) consists of an initiator and an electrolyte whereas the continuous phase (oil phase) contains monomer, surfactant, and crosslinker. The monomer is determined based on the material's desired hydrophilic/hydrophobic characteristics. Because vinylbenzyl chloride (VBC) is a hydrophobic monomer, for instance, the polyHIPE material produced from it additionally possesses hydrophobic properties [27]. Styrene and divinylbenzene (DVB) are the most favored monomers in terms of monomer stability and ease of use [22]. The type and amount of a surfactant have an impact on pore shape, monomer stability. One of the surfactants commonly used in the production of polyHIPE is Span 80. The addition of electrolyte material to the polymerization process was supposed to prevent Ostwald growth.

PolyHIPE materials are inherently low-surface-area materials. This is due to the fact that when the droplet phase is removed, depending on many factors, materials with very large pores are formed, as shown in Figure 2.4, and the pores are interconnected as the droplet phase thins the polymer wall [26].

In terms of cost of production, PolyHIPEs produced by emulsion molding with simple processes are also favorable. This is an advantage that broaden the range of applications for polyHIPE. One of these application areas is catalysts.

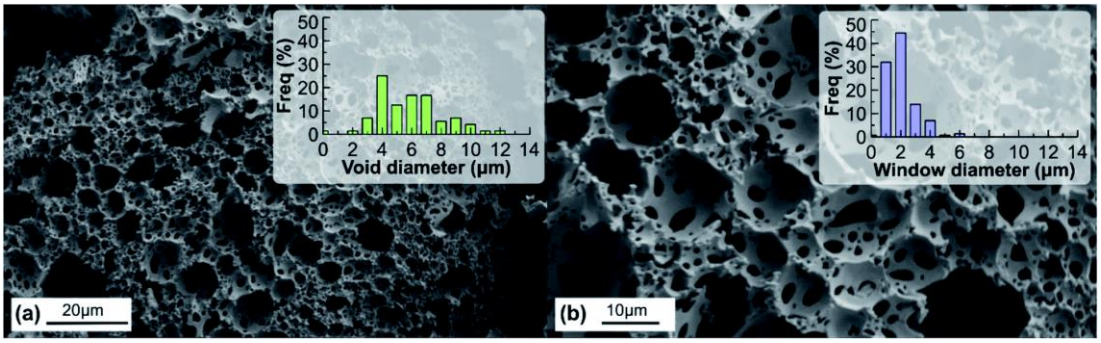

Figure 2.4 : SEM images of the polyHIPE obtained along with (a) void and (b) window diameter distributions.

PolyHIPE materials do not have catalytic active sites. Therefore, the PolyHIPE material may be functionalized to provide catalytic capabilities. In addition, it is aimed to make the catalyst more efficient by increasing the surface area of the polyHIPE material to be used as a catalyst. The surface area of the polyHIPE material can be enhanced by performing a hypercrosslinking process using crosslinking agents including DVB.

2.6 Hypercrosslinking

Hypercrosslink bonds are three-dimensional, rigid, and extended bonds obtained by crosslinking polystyrenic structures in an extended state using external crosslinkers [28]. Polystyrene network is also called Davankow-type resin, as it was first introduced by Davankov and Tsyurupa [29]. The process of crosslinking is frequently referred to as the Friedel-Crafts reaction [28]. The crosslinkers are crosslinked in this case by bridging the aromatic residues. The result is highly crosslinked materials with low packing density due to the rigid structure that keeps the polymer chains apart and high surface area due to the large number of small pores. These are known as hypercroslinked polymer materials.

2.7 Hypercrosslinked Polymers

In this method, the polymer is hyper-crosslinked via the Friedel-Crafts reaction with an external crosslinker in the presence of Lewis acid catalyst [30].

As shown in Figure 2.5, to obtain a hypercrosslinked polymer , a slightly crosslinked polymer swells in a solvent [29].

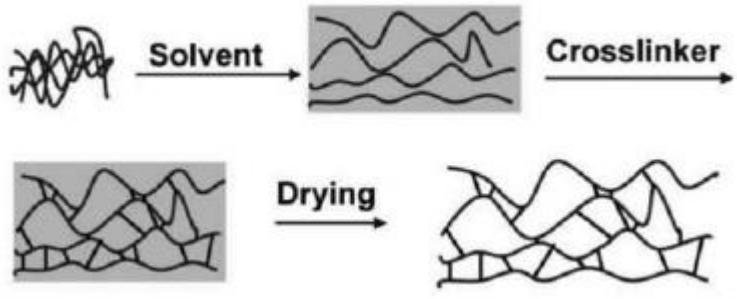

Figure 2.5 : Scheme of hypercrosslinking of polystyrene bonds.

In this material with expanded polymer chains, the crosslinking reaction takes place rapidly with the support of the catalyst. The solvent is then withdrawn from the system, and the solvent volume is converted to the pore volume. As a result, PolyHIPEs with interconnected pores and hierarchical pore structures are formed. Chemical modification methods can then be used to give these polyhyper materials different characteristics.

The polymer to be hypercrosslinked can be linear or slightly crosslinked. Polystyrene precursors are examples.

In this process, the solvent plays a crucial role as a significant parameter. Thermodynamically, the solvent needs to be compatible with the polymer to expand the free volume between polymer chains until it swells, ensuring compatibility between the polymer chains [29]. Dichloroethane (DCE) is generally preferred as a solvent because of its compatibility with polystyrene and also because it is compatible with the Friedel-Crafts reaction [28].

An example of a cross-linking agent is DVB, which is widely used in the industry as a cross-linking agent, can be homogeneous in distribution, and can form hard and short cross-links.

Friedel-Crafts reactions commonly prefer $FeCl_3$ as the catalyst due to its molecular size advantage as a Lewis acid, facilitating the overcoming of steric hindrance as solubility and bond formations occur [28]. The quantity of this catalyst used in the reaction is also highly significant. Excessive usage can damage the high specific surface area, whereas using it in small amounts can lead to decreased efficiency and a lower formation rate of the high specific surface area.

2.8 Characterization

The chemical composition, atomic structure, particle shape and size, pore interconnectivity, pore size and distribution, and surface area of the catalyst material all influence its catalytic activity, selectivity, and durability. As a result, following catalyst production, several characterization tests should be performed on the catalyst to assess whether it is suitable for the purpose.

2.8.1 BET (Brunauer–Emmett–Teller) surface area measurement

It is a technique used to investigate the pore structure of a catalyst with micro, meso and macro pore structure and to determine its surf ace area. This technique is usually measured by inert gas N_2 sorption and Hg intrusion techniques [31]. N_2 sorption isotherms are preferred in a catalyst material with a hierarchical pore structure since N_2 can enter micropores and mesopores more easily than Hg. These gases are adsorbed on the surface of the material, and interactions with the surface take place. N_2 isotherms show the relationship between the molecule adsorbed per unit mass of solid surface and the relative pressure (p/p_0) due to these interactions at a given temperature. The amount of this adsorbed gas is expressed as the volume or mass of adsorbed gas per unit mass of solid adsorbent. In this way, the surface area of the material can be calculated. This method using N_2 sorption isotherms is called surface area analysis or BET analysis. In order to perform BET analysis, at least 200-300 mg particles should be used [31]. This gas adsorption determines the pore size and, therefore, the surface area.

2.8.2 Fourier transform infrared spectroscopy (FT-IR)

The Fourier Transform Infrared (FT-IR) analysis method can be used to follow the reactions taking place in catalyst synthesis and to detect the presence of functional groups. It is a very practical and short-term characterization technique. This technique is realized by measuring the vibrational motions of chemical bonds in the material with absorbed infrared spectra (IR) [32]. The change in vibration in these chemical bonds and the absorbed IRs cause the formation of spectral peaks. The peaks are specific for each functional group. As a result, we can obtain information about the molecular structure of the material with this method.

2.8.3 Scanning electron microscopy (SEM)

It is a characterization method defined as an elemental mapping technique used to study the pore structure and distribution of porous material [32-33]. With this analysis, the surface structure of the catalyst is examined. In this technique, the material is scanned with a high-energy electron beam, thus providing interaction between the material and the electron beam and generating some signals from the surface by the backscattered electrons and secondary electrons, and these signals are converted into images by the scanning electron microscopy (SEM) method. In this way, information about the particle size distribution of the catalyst, phase transitions, and the chemical composition of the surface is provided.

2.9 Application Areas of PolyHIPE Materials

PolyHIPEs' low density, hierarchical porous structure, ability to be produced in both homogeneous and heterogeneous phases, and ability to acquire several desirable functional properties through particular chemical reactions after-production are among their many advantages that expand their potential applications. PolyHIPEs are used as catalysts, membranes, absorbents, and support materials [34].

Permeability, selectivity, and durability are critical characteristics in membrane design. To improve the selectivity of the PolyHIPE material for membrane applications, the internal phase ratio should be improved, and the density should be enhanced to improve its durability. All of this must be done while maintaining a specific amount of permeability. It may therefore be utilized as a gas separation membrane. In a previous research, a membrane for CO_2 collection was developed by combining polyHIPE owing to its hierarchical pore structure with MOF (metal organic framework) for its high surface area [35]. Polyethylenimine (PEI) amine groups were used to promote CO_2 selectivity. As a result, a high permeability and selectivity polyHIPE/MOF membrane was developed.

PolyHIPEs' high porosity structure, interconnectivity of the pores, large surface area and volume, and biodegradability indicate that they are suited for application in tissue engineering. Porosity is essential in skeletal structure for reasons such as nutrition delivery and cell growth. In this aspect, skeleton-like materials can be produced with adjustable interconnected pore sizes with polyHIPE obtained by the emulsion-

templating method. The biocompatibility of the monomer employed in the manufacture of polyHIPEs is another significant and crucial aspect here. In a research study, thiol- and polycaprolactone-based polyHIPE were developed [36]. In this way, cell attachment and viability were supported by obtaining biodegradable polyHIPE.

PolyHIPE materials have all of these characteristics, allowing them to be used as templates for the synthesis of porous carbons and porous ceramics, which may be used as well as membrane supports, separation materials, and absorbents.

By integrating catalytic features along with particular functionalizations, polyHIPE materials can be used as catalysts. In a previous study, graft polymerization of terbutyl acrylate with chlorine initiation sites on polyHIPE was carried out to add Brønsted acid sites (BAS) to the obtained polyHIPE material [26]. As a result, functionalized polyHIPE material was developed. In this research, carboxylic acid-functionalized polyHIPE was produced by further hydrolysis. Basic polyHIPE, on the other hand, was synthesized by graft polymerization with glycidyl methacrylate (GMA), followed by modification with diethylamine. The objective of this research is to highlight the energy efficiency and reusability of both acidic and basic heterogeneous polyHIPE materials. After synthesizing the polyHIPEs, characterization and test results showed that the separately-synthesized polyHIPEs performed much better than commercial resin-based materials. SEM images additionally demonstrated that the functional groups attached to the polyHIPE had no effect on the hierarchical pore sizes.

In a study by Zhang et al., the hierarchical pore structure of polyHIPE material was utilized due to its rapid diffusion. In this way, the conversion reactions of large molecules such as carbohydrates to other molecules have been achieved in a single container [37]. In this study, cellulose was converted to hydroxymethylfurfural (HMF) in the presence of an acid-base catalyst (SPHs@MSNs-SO_3H-NH_2) in a one pot. The catalyst was developed by the emulsion templating approach. The catalyst structure contains mesoporous silica nanoparticles (MSNs-SO_3H-NH_2) which provide acid-base functionality. Sulfonation was used to develop a catalyst with hierarchical porosity. This hierarchical structure promoted cellulose diffusion in the cellulose conversion reaction. Furthermore, the size of the surface area facilitated the transport of a large molecule particle such as cellulose to the deepest depths in the catalyst. Consequently, HMF was produced with a 44.5% yield.

Another study used a heterogeneous acid-base catalyst to synthesize selective HMF from glucose in a one-pot reaction [38]. The use of an acid-base catalyst in this research is intended to shorten the HMF production processes. Isomerization of glucose to fructose was achieved with the base catalyst, and dehiscration of fructose to HMF was achieved with the acid catalyst. By avoiding side reactions, more efficient HMF was produced in one pot, in a more environmentally friendly approach, and in a shorter period of time.

There are studies on the use of polyHIPE materials as adsorbent materials due to their high porosity. Methylene blue (MB), a cationic dye that is extremely damaging to ecology and the environment, is widely used in textiles and healthcare applications. Considering that tons of dyes are discharged directly into water systems every year, many technologies have been developed to remove pollutants such as MB from water. In this context, the emulsion templating method was used to develop adsorbents with carboxylic acid groups which possess selective properties due to their easy functionalization, a high surface area due to their highly porous structure, and are sustainable due to their reusability [39]. In order to increase the surface area of the polyHIPE material obtained in the study, hyper-crosslinking was performed through alkyl chloride groups. When the analysis results of the non-HIPER-crosslinked and HIPER-crosslinked polyHIPE adsorbents were compared, it was observed that the HIPER-crosslinked adsorbent performed better due to its higher surface area. The maximum adsorption capacity for MB was found to be 450 mg/g.

Porous polyhHIPE materials can also be used as support structures in biodiesel production. In a study by Dizge et al., the styrene-divinylbenzene-polyglutaraldehyde (STY-DVB-PGA) copolymer produced via the emulsion templating method was used as a support for lipase immobilization [4]. In this study, the copolymer support material was able to immobilize large amounts of protein structures thanks to its porous structure due to the production method, was functionalized with PGA, and was able to immobilize enzymes by both physical and chemical adsorptions. In this method, biodiesel could be obtained from canola oil with 97% efficiency in the presence of lipase immobilized on the STY-DVB-PGA copolymer.

In another study by Dizge et al. polymeric biocatalysts in styrene, DVB and PGA structure containing aldehyde functional groups in different forms were obtained using PolyHIPE method and used as immobilization support for lipase molecule from

sunflower oil, soybean oil and waste oils to obtain biodiesel [40]. As a result of the study, 97% yield of biodiesel was obtained from sunflower oil.

3. EXPERIMENTAL PART

3.1 Materials and Instruments

3.1.1 Materials

Vinylbenzylchloride (Fluka), DVB (Fluka), were passed through alumina column to remove inhibitors. $FeCl_3$ (anhydrous), $CaCl_2$ (anhydrous, 97%) and $K_2S_2O_8$ were used as received. Nitric acid (65%, Merck), Isopropyl alcohol (IPA; technical grade), Acetone (technical grade), Ethanol (95 %, Carlo Elba), Oleic acid (≥99% (GC); Sigma).

3.1.2 Instruments and methods

The polyHIPEs were characterized by SEM (FEI-Philips XL30 Environmental Scanning Electron Microscope with Field Emission Gun (Equipped with EDAX-Energy Dispersive X-ray Analysis Unit) operating at 10.0 kV to observe the surface morphology. The samples were prepared by dispersing the powder onto a double-sided adhesive surface. To study the surface area and porosity of polyHIPES nitrogen adsorption isotherms were measured at -196°C using a Micromeritics TriStar II 3020 Surface Area and Pore Size Analyser. Prior to measurement, the samples were degassed for 12 h at 100°C. The average pore size was determined using the Barrett−Joyner−Halenda (BJH) method. Functional groups of the polymers were confirmed by FT-IR spectroscopy (Thermo Scientific, Nicolet iS20) in the range between 4000-450 cm^{-1}.

3.2 Preparation of Solid Catalysts by Emulsion Template Method

In this thesis, emulsion templated polymers were prepared, hypercrosslinked and functionalized to obtain solid acid catalysts for oleic acid esterification. A 3-step-modification was applied to obtain sulfonic acid on the surface of crosslinked polymer and the resulting polymeric material was used to catalyze the reaction between oleic acid and methanol.

3.2.1 High internal phase emulsions (HIPEs) and polyHIPEs

HIPEs with 90% pore volume were prepared. The initial emulsion was composed of 10 mL organic or continuous phase and 90ml water or internal phase. A 250 mL round-bottomed flask was charged with VBC (8 mL), DVB (2 mL) as crosslinker and surfactant Span 80 (200 mg) with an overhead stirrer fitted with a D-shaped polytetrafluoroethylene (PTFE) paddle. The resulting mixture was purged with nitrogen gas for a period of 15 min. The internal phase (water phase) was prepared by dissolving 0.2 g potassium persulfate and 1.0 g calcium chloride in 90 mL de-ionised water and the resulting solution was purged with nitrogen for 15 min. The internal phase was then added to the organic phase in a dropwise manner for 30 min under constant mechanical stirring at 300 rpm. Once the addition of the aqueous phase was completed mechanical stirring was continued for 1 h at 300 rpm to produce a homogeneous emulsion and at 50 rpm to remove any entrapped air bubbles. At the end of the process very viscous emulsion (HIPE) was obtained and it was then transferred to the mold (polyethylene terephthalate (PET) container) and cured at 60^{o}C for 48 h. To remove surfactant and polymerization impruties polyHIPE in the shape of monolith was extracted by Soxhlet extraction with distilled water and IPA, both for 24 h, then dried in vacuo for 24 h.

3.2.2 High-surface-area polymers: preparation of the hypercrosslinked polyHIPE (HXL-PHP)

PolyHIPE's with 90% pore volume were were hypercrosslinked to obtain high-surface-area polymers: Initially the monolith polyHIPE's were powdered using a mortar and pestle for a uniform reaction mixture. 1 g powdered VBC polyHIPE was placed in a 250 mL 3 necked round bottom flask and 50 mL DCE was added to the flask. One of the necks was fitted with rubber septum and the other two were fitted with glass stopper, and a reflux condenser was attached to one of them. The mixture was degassed through a needle under a stream of nitrogen for 15 min with 300 rpm stirring rate. When then nitrogen flow was removed the flask was left with stirring for a further 45 min to let the polymer swelled. Then the flask was placed in an ice bath and anhydrous 1.09 g $FeCl_3$ was added to the flask through the neck of the flask quickly. The flask was then degassed again for a period of 15 min. Once the nitrogen supply was removed the flask was left stirring for a further 45 min in the ice bath to

make sure that a uniform dispersion of $FeCl_3$ was achieved. The sealed flask was allowed to reach a room temperature. Next, the flask was placed in an oil bath at 80°C to start Friedel Crafts reaction for 15 min. To control the reaction, the excess ethanol was added at the end of the given set time and then filtered under vacuum. The resultant 15min/60min HXL-PHPs were washed with ethanol (3x40 mL) and 0.1 M $HNO_{3(aq)}$ (3x40 mL). A further soxhlet extraction in acetone for 10 h (15 cycle) was performed and the HXL-polymers were left in oven for drying at 60°C.

3.2.3 Modification step 1: converting surface benzyl chloride groups to benzyl thiouronium salts

The surface benzyl chloride groups of polyHIPE were converted to thiouronium salts in ethanol. 0.13 M thiourea solution was prepared by dissolving 3.29 g thiourea in 100 mL absolute ethanol and this solution was added to a 250 mL round bottom flask. And then 1.0 g overnight-heated powder polyHIPE (5.5 mmol functional group) were added to this flask. The flask was sealed and heated to 40 °C for 24 h while stirring at 250 rpm. At the end of the reaction the mixture was filtered under vacuum and washed with ethanol (3x20 mL), distilled water (3x20 mL), ethanol (3x20 mL) and then left in a conventional oven for drying at 60°C. The resulting polymer was characterized by FT-IR to confirm the surface benzyl thiouronium salts. The procedure was repeated for the hypercrosslinked polyHIPE (HXL-PHP) prepared by hypercrosslinking reaction for 15 min (HXL-15min-PHP).

3.2.4 Modification step 2: tailoring polyHIPE surfaces with thiol groups

To convert benzyl thiouronium salt groups on polyHIPE surface to thiol functionality, 1 g powdered polyHIPE with benzyl thiouronium salts (overnight-heated) was placed in a 100 mL round bottom flask and 40 mL, 0.25 M NaOH aqueous solution was added onto the polymer. The mixture was stirred for 8 hours at room temperature. At the end of the reaction the mixture was filtered and washed with 0.1 M HCl (3x20 mL) and distilled water until the pH of the washing solutions becomes neutral. And then, the porous polymer was dried for 24 hours at 60°C in a conventional oven. The resulting polymer was characterized by FT-IR to confirm the surface benzyl thiouronium salts. The procedure was repeated for the benzyl thiouronium salts functional HXL-PHPs prepared in 9.2.3.

3.2.5 Modification step 3: obtaining solid catalysts with sulfonic acid groups

The polymer surfaces were tailored with sulfonic acid groups by oxidation of thiol groups. 1 g powdered polyHIPE with thiol groups (overnight-heated) was placed in a 250 mL round bottom flask fitted with a condenser and 100 mL of hydrogen peroxide-acetic acid solution (40/60, v/v) was added onto the polymer. The mixture was stirred at room temperature for 12 h. At the end of the reaction the mixture was filtered and washed with excess water. And then, the porous polymer was dried for 24 h at 60ºC in a conventional oven. The resulting polymer was characterized by FT-IR to confirm the surface benzyl thiouronium salts. The procedure was repeated for the HXL-PHP prepared by hypercrosslinking reaction for 15 min (HXL-15min-PHP).

3.3 The Preparation of Sulfonated PolyHIPE

The preparation of solid acid catalyst was carried out as follows: Mononers, Styrene (8 mL), DVB (2 mL) and Span 80 (0.2 g) as surfactant was placed in a 250 mL round-bottomed flask with an overhead stirrer fitted with a D-shaped PTFE paddle. The resulting mixture was purged with nitrogen gas for a period of 15 min. For the preparation of the internal phase, 0.2 g potassium persulfate and 1.0 g calcium chloride were dissolved in 90 mL de-ionised water and this solution was purged with nitrogen for a period of 15 min. And then, the organic solution was stirred under nitrogen at 300 rpm and the aqueous internal phase was added for a peried of 30 min under constant mechanical stirring in a dropwise manner. Once the addition of the aqueous phase was completed mechanical stirring was continued for 1 h at 300 rpm to produce a homogeneous emulsion and at 50 rpm to remove any entrapped air bubbles. At the end of the process very viscous emulsion (HIPE) was obtained and it was then transferred to the mold (PET container) and cured at 60ºC for 48 h. To remove surfactant and polymerization impruties polyHIPE in the shape of monolith was extracted by Soxhlet extraction with distilled water and IPA, both for 24 h, then dried in vacum for 24 h.

3.4 Functional Group Content Determination

The sulfonic acid contents of solid acid polyHIPE catalysts were determined by acid-base back titration. For this purpose, 50 mg of the polymer sample was left in contact

with 10 mL 0.1 M $NaOH_{(aq)}$ with constant stirring for 24 h at room temperature. After filtration, 1 mL of each filtrate was transferred into 10 mL flask and the sulfonic acid contents of the polymers were determined by titration with 0.01 M HCl solution in the presence of phenolphthalein indicator.

3.5 Chlorine Content Determination

The chlorine content of porous polymers was measured by mercury(II) thiocyanate method [41]. 200 mg polyHIPE was places in a 100 mL round bottom flask and 20 mL NaOH/EtOH (10%, w/v) solution containing 1 mL distilled water was added into this flask. The mixture was heated at reflux temperature for 5 h. And then the mixture was cooled down to room temperature and filtered under gravity. The solution was diluted and 10 mL aliquot of the chloride solution in a 25 mL was placed in a graduated flask and 2.0 mL of 0.25 M ammonium iron(III) sulphate [$Fe(NH_4)(SO_4)_2,12H_2O$] in 9 M nitric acid was added into the flask followed by addition 2.0 mL of a saturated solution of mercury(II) thiocyanate in ethanol. After 10 min, the absorbance of the sample solution and also of the blank was measured by UV spectrophotometer at 460 nm. The amount of chloride ion in the sample corresponds to the difference between the two absorbances and is obtained from a calibration curve. The calibration curve was constructed by using a standard sodium chloride solution containing 10 μg Cl^- / mL covering the range 0-50 μg.

3.6 Catalyst Testing

Catalyst testing was carried out using different types of polyHIPEs. We had two main purpose to perform the catalysis experiments: Firstly, the high catalyst yield and the enhanced reaction kinetics for esterification reaction between methanol and oleic acid and secondly, proving the advantage of polyHIPE catalyst with methylene bridge. On the basis of these purposes three different type of sulfonic acid functional polyHIPE were prepared and used in catalyst testing.

3.6.1 Catalytic performance of polyHIPEs

Catalytic reactions were performed in a 100 mL round-bottomed flask. In a typical run, the polyHIPE catalyst containing 5 mmol acid functional groups was mixed with the catalyst containing 50 mmol oleic acid and 450 mmol methanol. The mixture was

stirred at 90^{o}C for 3 h and then centrifuged at 5000 rpm for 5 min. The liquid phase was evaporated to remove methanol and by-product water and the acid value of remaining part was analysed by titration. The activity of the catalyst was determined by the reduction of acid value during the esterifaction reaction (3.1):

$$\eta = A_{in} - A_{out} / A_{in} \times 100\% \quad (3.1)$$

where A_{in} and A_{out} are acid values of the initial and final oleic acid respectively, mg KOH g^{-1}.

The acid values were measured according to the following procedure: The sample is made of oleic acid was dissolved in 2-propanol and titrated with the 0.1 mol/L potassium hydroxide (ethanol) solution. The oleic acid value is calculated from the titration volume.

3.6.2 The reusability

To investigate the catalyst reusability, esterification reaction between methanol and oleic acid was carried out with 4 cycles under the same optimum conditions. After each run, the catalyst was separated from reaction mixture through filtration under gravity and washed with excess methanol. And the catalyst was dried in a conventional oven at 60^{o}C for 24 h and was re-used for the next run.

4. RESULTS AND DISSCUSSION

Acid catalysts have been widely used in petrochemical industry, biomass conversion and the production of fine chemicals. These catalysts are mostly homogenous catalysts like Bronsted acids. The recent attention to a sustainable society has led a great effort to prepare solid acid catalysts to replace the traditional liquid acids. Heterogeneous acid catalysts have advantages over homogenous catalysts: The active acidic groups are bounded to a matrix so they cannot be released causing environmental issue and corrosion in equipment. They can be re-used many times due to the insolubility of matrix structure. Naturally, solid acids show hydrophilic character. Many reactions use water as solvent and also water is a byproduct. Water can be adsorbed solid acids and deactivate catalytic sites. Water is a byproduct in esterification reaction and it can poison the active acid groups [42]. A solid acid with some degree of hydrophobicity can overcome this problem and enhance its catalytic activity and reusability [43].

This thesis covers the preparation and catalytic application of polymeric solid acid catalysts. The thesis has two main purposes:

i. To obtain an interconnected, open-porous, high-surface-area acid catalyst and use it in esterification reaction between methanol and oleic acid.
ii. To tailor solid acid surface with sulfonic acid catalytic groups which has resistance against deactivation through the methylene bridge and a sufficient hydrophobicity.

All catalysts in this thesis were prepared by emulsion-templated method as porous polymers. Porous polymers are versatile materials which have been widely used as adsorbents. PolyHIPEs are porous polymers having open-porous cellular structure with interconnected pores. They are hierarchically porous with large pores allowing adsorbates to the functional groups located inside the pores by mass transfer rather than diffusion.

4.1 Emulsion Templated High-Surface-Area Sulfonic Acid Functional Porous Polymers

High-surface-area polymeric catalysts with sulfonic acid groups were prepared using emulsion templated method. For this purpose, were prepared using VBC, DVB and span80 as organic phase and water including $K_2S_2O_8$ and $CaCl_2.2H_2O$ as water phase. We choice VBC monomer for two reasons:

i. It has a methylene chloride group which acts as an internal crosslinker in Friedel Crafts reaction to obtain high surface area polymers.
ii. Through hypercrosslinking reaction, which is a controlled reaction, it is possible to remain unreacted alkyl chloride groups which can be converted to sulfonic acid groups.

By this strategy, we obtained both high-surface-area and functional porous polymers. DVB is a crosslinker and it was used as 10% (mol%) of the total monomer phase. It is necessary to use a crosslinker to obtain a polyHIPE scaffold through enhancing the emulsion stability. It is a fact that polyHIPEs possess mainly macro pores (pores larger than 50nm), their surface areas are originally low (6-10 m2/g) which can cause slow reaction rates. To overcome this drawback, polyHIPEs were hypercrosslinked through Friedel-Crafts alkylation reaction catalyzed by a Lewis acid $FeCl_3$ and high-surface-area porous polyHIPEs were prepared.

To prepare HIPE, the continuos phase (monomer phase: VBC, divinybenzene, and surfactant span 80) and water phase (distilled water, initiator $K_2S_2O_8$ and electrolyte $CaCl_2.2H_2O$) were prepared separately. The pore volume of the HIPE was 90%. The water phase was added to the organic phase slowly and by the polymerization of monomer phase a low density, permeable, highly porous material namely polyHIPE was obtained Figure 4.1. The surfactant span80 stabilizes the emulsion and also it is necassary to obtain an open-porous, interconnected network. During the curing the polymer walls in droplets becomes thinner and eventually pores form between droplets (windows) [44]. Therefore it is crucial to use a proper amount of surfactant to make sure that the resulted polymer has an intrconnected porous structure. Span 80 was 20% (m/m) of organic phase. The higher amounts of span80 causes closed-pore porous polymer [45]. After removing the droplet phase by drying, the large pores (voids) and the interconnecting pores (windows) are formed. The pore diameter is controlled

through variation of HIPE droplet diameter, and the surface can be functionalised chemically.

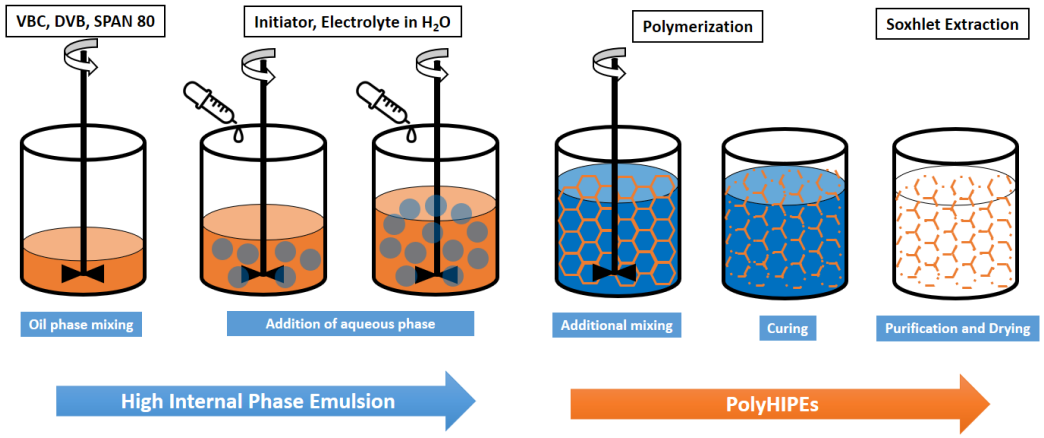

Figure 4.1 : Preparation of polyHIPE.

4.2 Preparation of Solid Acid Catalysts

Solid acid catalysts were prepared by a five-step procedure:

i. The first step is the preparation of a HIPE which has an external (organic) phase of VBC and DVB followed by curing the external phase to obtain polyHIPE material as a support for solid acid catalyst.

ii. The hypercrosslinking reaction catalyzed by $FeCl_3$ through methylene chloride groups to increase the surface area of polyHIPE (Figure 4.2).

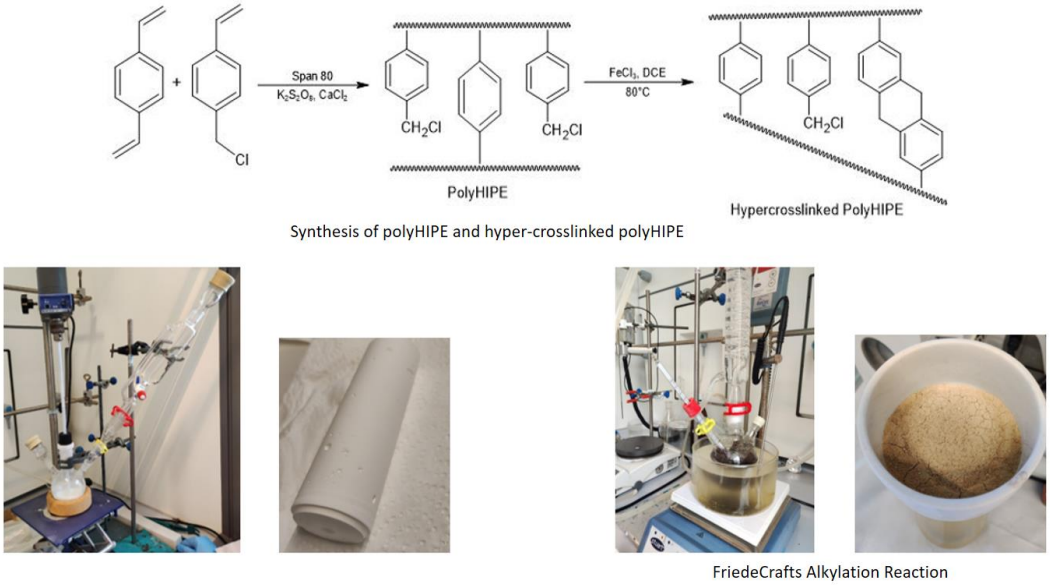

Figure 4.2 : Preparation of HXL-PHP.

iii. The conversion of methylene chloride groups to thiouronium salts using the unreacted methylene chloride groups.

iv. The obtaining thiol groups on the polyHIPE surface.

v. The conversion of the thiol groups to sulfonic acid groups (Figure 4.3). As a result of this strategy, a high-surface-area polyHIPE with sulfonic acid groups was obtained.

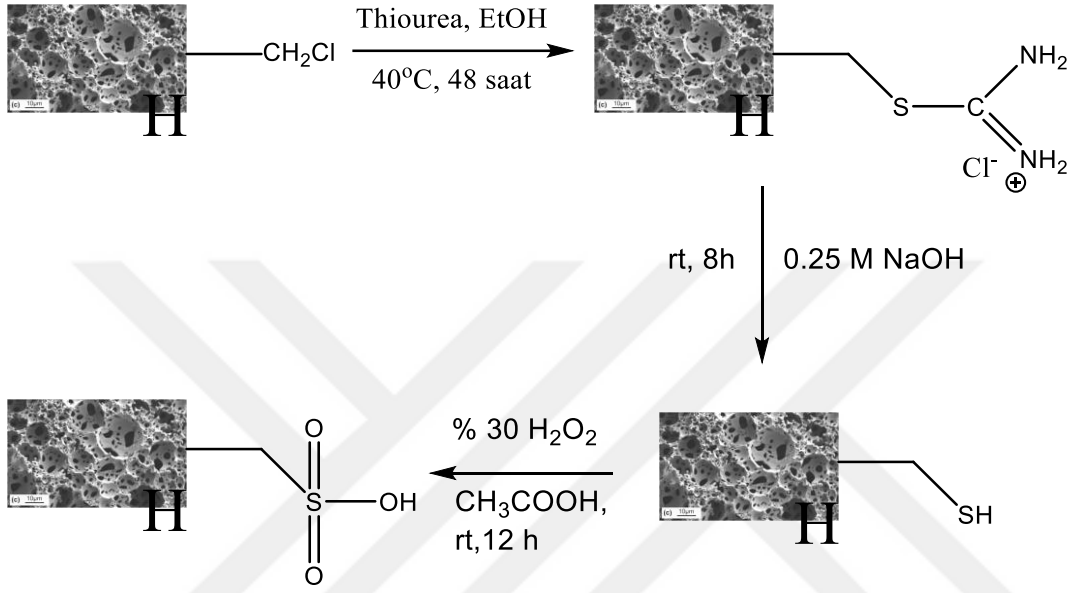

Figure 4.3 : Preparation of sulfonic acid functional HXL-PHP.

The HXL-PHP was prepared with the hypercrosslinking reaction for 15 minutes. The hypercrosslinking reaction is a controlled reaction so it was possible to increse the surface area for 15 min while remaining some unreacted metheylene chloride groups for surface modification. The hypercrosslinking reaction was applied through Friedel-Crafts alkylation reaction catalyzed by a Lewis acid $FeCl_3$ where chloromethyl group acts as an internal electrophile, and dichloroetane (DCE) as solvent and external crosslinker (Figure 4.4). DCE has a boiling point of 80^0C so this solvent both allows the reaction take place at high temperatures and also acts as an external crosslinker for the hypercrosslinking reaction. As a result of this reaction micro- and mesopores are added into the framework and high specific surface areas can be obtained. As the reaction proceeds, the methylene bridges form between the monomer units of VBC, and DCE as an external crosslinker can be involved in the bridge forming as well. Also, the formation of a six membered ring between two methylene chloride is seen as a characteristic of the hypercrosslinking of VBC based polymeric precursors (Figure 4.5).

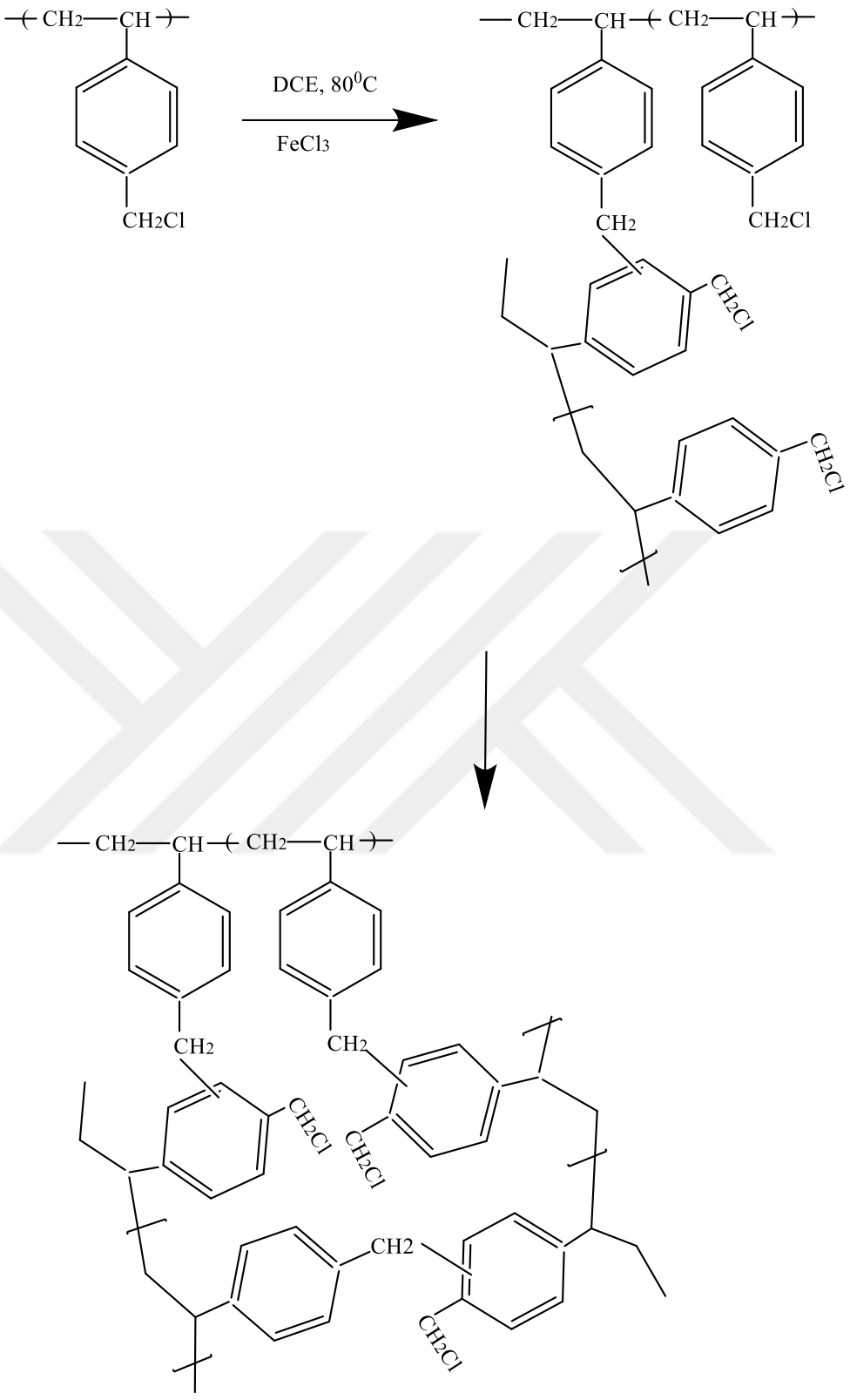

Figure 4.4 : The hypercrosslinking reaction through Friedel-Crafts alkylation catalyzed by a Lewis acid $FeCl_3$.

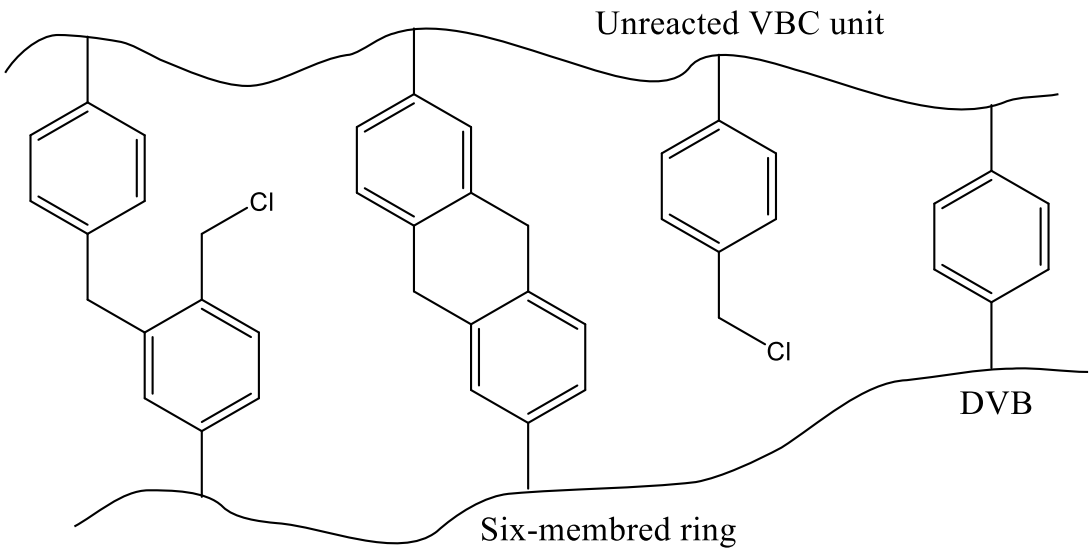

Figure 4.5 : The probable crosslinking formations in the HXL-PHP.

We can observe in Figure 4.5 that the hypercrosslinking reaction introduces the additional crosslinks together with DVB. It is a controlled reaction so some VBC groups can remain unreacted.

This thesis assumes that the methylene bridge between polymeric network and sulfonic acid group can enhance the re-use property of the solid acid catalyst. This methylene bridge prevents the cleavege of sulfonic acid groups during biodiesel production and the solid acid catalysts will not lose the functional group capacity. Moreover, tailoring the surface of solid catayst in a controlled way can make the catalysts hydrophobic sufficiently. To prove this hypothesis, a polyHIPE was prepared by using styrene and DVB instead of VBC. And then, the aromatic groups were sulfonated by chlorosulfonic acid (Figure 4.6). In this way, we could observe the effect of methylene bridge and hydrophobicity of the solid catalyst. The sulfonation reaction is not a controlled reaction so it is not possible to control the hydrophobicity of the solid catalyst.

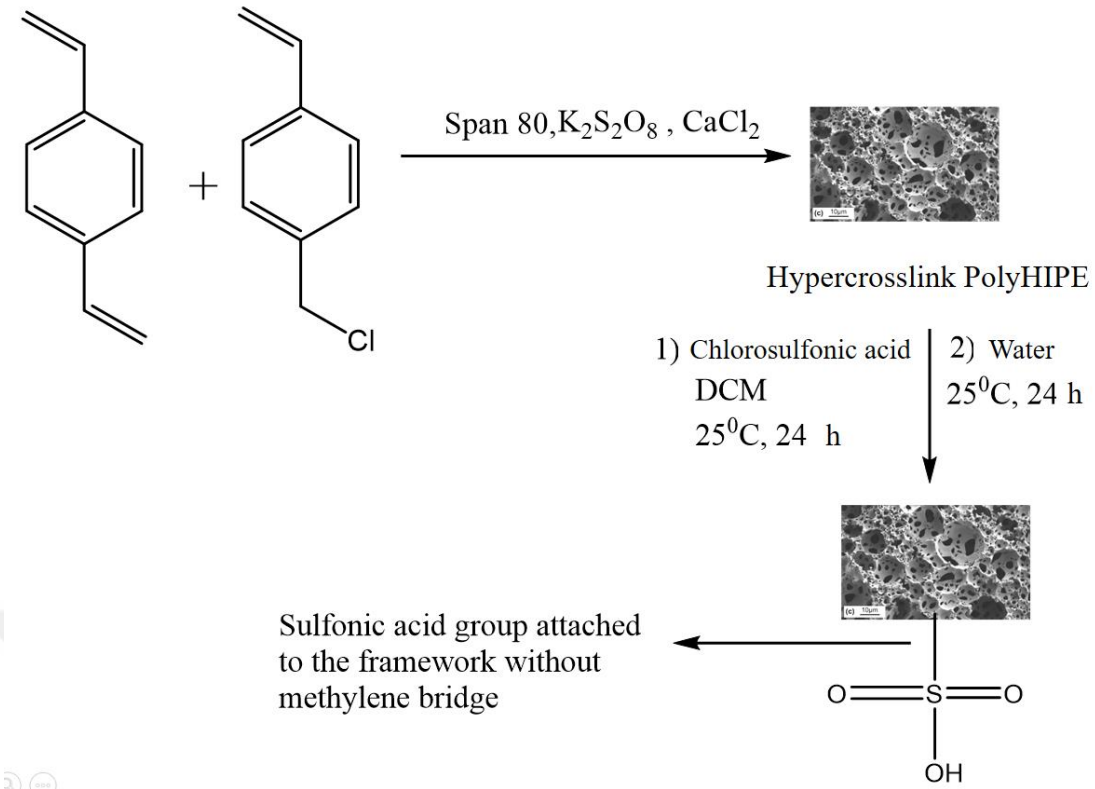

Figure 4.6 : Sulfonation of the HXL-PHP.

4.3 Characterization of Solid Acid Catalysts

The solid acid catalysts were characterized by the following methods: The surface morphology of the polyHIPE solid catalysts were examined by Scanning Electron Microscopy (SEM). The surface area and pore sizes were measured by BET. The surface functional groups were determined qualitatively by FT-IR and quantitatively by acid-base back titration. PolyHIPE morphology is complex so the terminology created by Cameron and Barbetta was used [46]**.** They defined the large spherical pores as voids which form during the vaporization of water internal phase and the smaller pores which interconnects voids as windows. Interconnected pores are formed where monomer films between droplets walls become thinner and eventually windows are produced on polymerization at a critical level of surfactant. The mezo- and micropores are formed on the polymer walls. The hierarchical pore structure of polyHIPE material can be clearly seen in Figure 4.7.

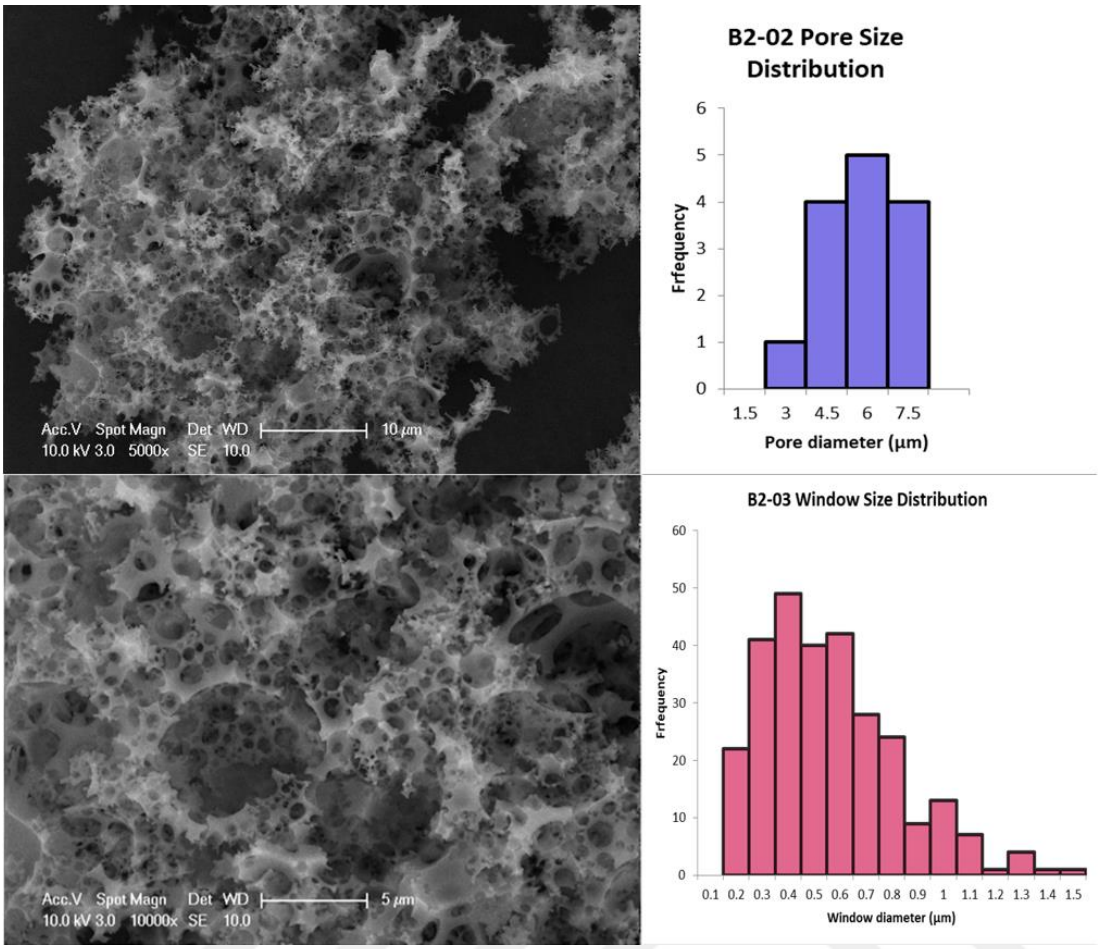

Figure 4.7 : SEM image and void and window size distribution of VBC polyHIPE.

The SEM image proves that the emulsion-templated porous polymer prepared in this thesis have a typical polyHIPE morphology which contains macropores, voids and windows. The porous polymers were prepared with 90% porosity with voids and windows having a narrow diameter distribution. The void and interconnected pore distribution were studied by image analysis [47]**.** The surface porosity analysis, based on an average void and average interconnecting window diameters as seen in Figure 4.7, was analyzed by ImageJ software statistically [48] using a number of SEM images taken from the each sample. As can be seen from Figure 4.7, the surface morphology characteristics of each sample was sustained all over the frameworks. To obtain the results that represents the surface morphologies of the samples, an average diameter analysis was carried out with the datasets of 282 windows, while this dataset was limited with 14 counts for voids. The ratio of the average window diameter to average void diameter (⟨d⟩/⟨D⟩) is an indicator for the interconnectivity of open-porous network of polyHIPEs. Here, the average void and window diameters of polyHIPE precursor were found to be 5.12 µm and 0.52 µm, respectively.

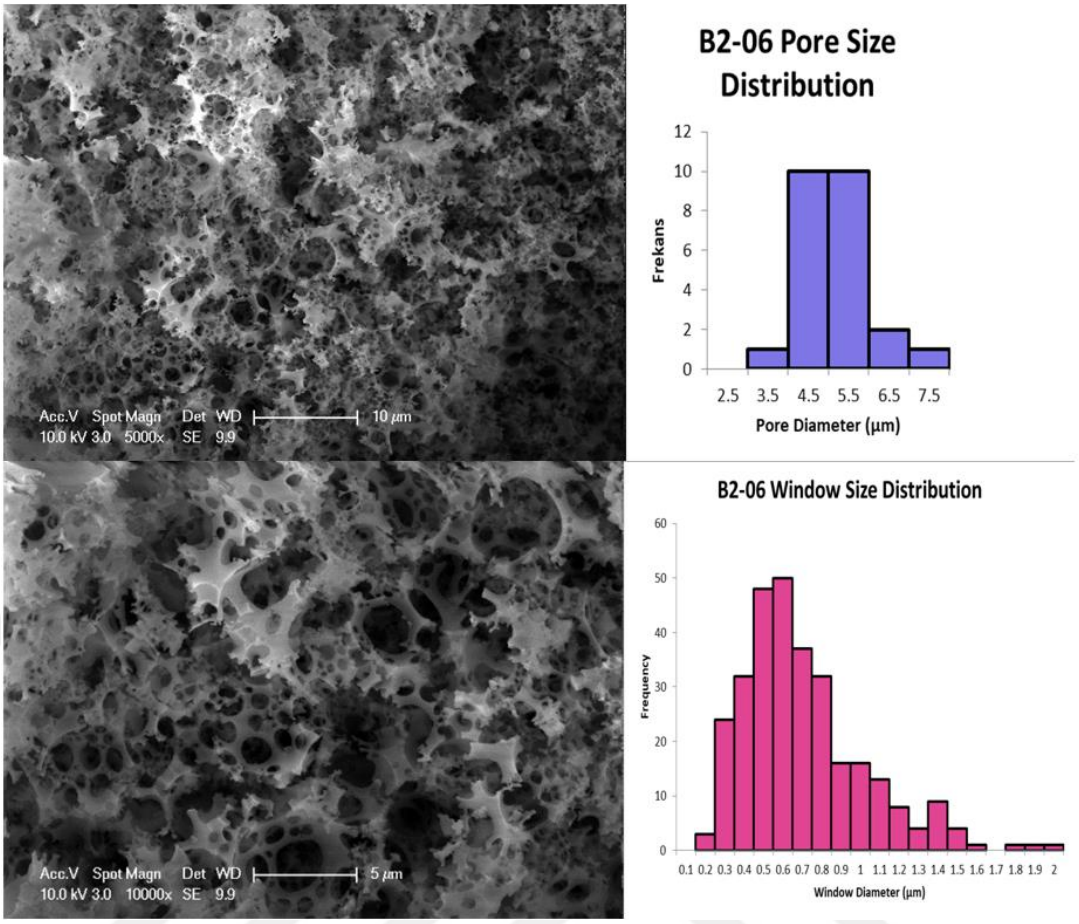

Figure 4.8 : SEM image and void and window size distribution of HXL-PHP.

The hypercrosslinked polyHIPSs (HXL-PHPs) were also examined by SEM. It can be seen in Figure 4.8 that the hypercrosslinking reaction for 15 min caused a decrease in the void size from 5.12 µm to 4,59 µm. however, the average interconnecting window size of PolyHIPE precursor increased from 0.4 µm to 0.66 µm (Figure 4.8). Introducing sulfonic acid groups to the surface of HXL-PHP did not have a significant difference on surface morphology (Figure 4.9). The average window and void diameters of HXL-PHP-SO_3H were found as 6.23 µm and 0.59 µm. It was an expected outcome that the hypercrosslinking reaction and surface functionalization did not have a significant effect on surface morphology in terms of ⟨d⟩/⟨D⟩ indicating the similar interconnectivity. The average diameter of interconnecting windows (⟨d⟩) and voids (⟨D⟩) as well as the degree of interconnections (⟨d⟩/⟨D⟩) of polyHIPE materials are summarized in Table 4.1.

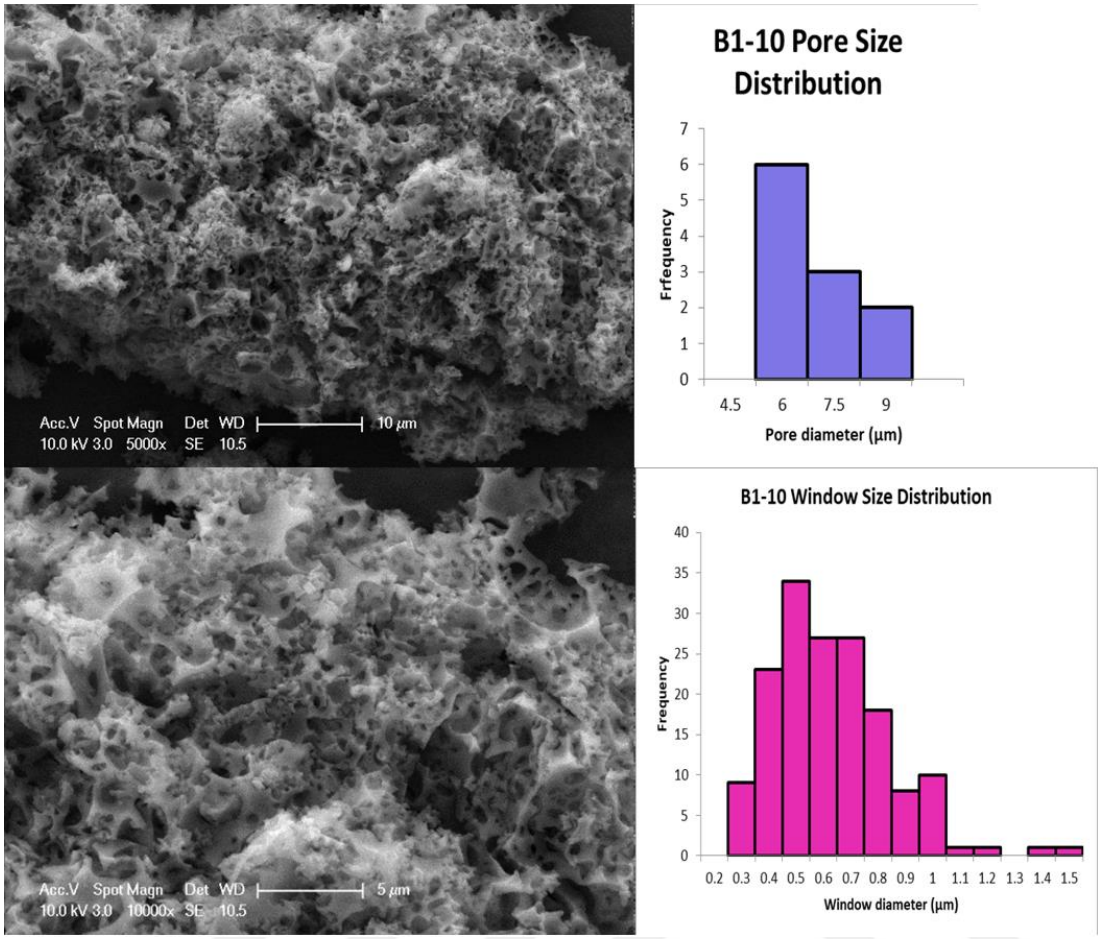

Figure 4.9 : SEM images and void and window size distribution of HXL-PHP-SO_3H.

The esterification reaction is catalyzed by surface sulfonic acid groups bounded to the polymer network. Identifying the functional groups is a crucial point of this study. The surface sulfonic acid groups were determined qualitatively by FT-IR and quantitatively by acid-base back titration. The FT-IR spectra of PolyHIPE (Figure 4.10), thiouronium salt functional PHP (Step 1 in Figure 4.10), thiol functional PHP (Step 2 in Figure 4.10) and sulfonic acid functional PHP (Step 3 in Figure 4.10) can be seen below.

Table 4.1 : BET surface area, pore and micropore volume, pore size, window size and interconnection values of polyHIPE and HXL-15min-PHP.

Sample ID	From BET measurements				From SEM Images		
	S_{BET} (m^2/g)	V_p (cm^3/g)	Avarage pore size[1] (nm)	Micropore volume (cm^3/g)	<d> (μm)	<D> (μm)	<d>/<D>
PolyHIPE	10.46	0.025	5.17	*[2]	0.52	5.12	0.102
HXL-15min-PHP	257.1	0.316	4.84	0.0485	0.66	4.59	0.143

[1] Based on BJH Adsorption

[2] The micropore area and micropore volume are not reported because either the micropore volume is negative or the calculated external surface area is larger than the total surface area.

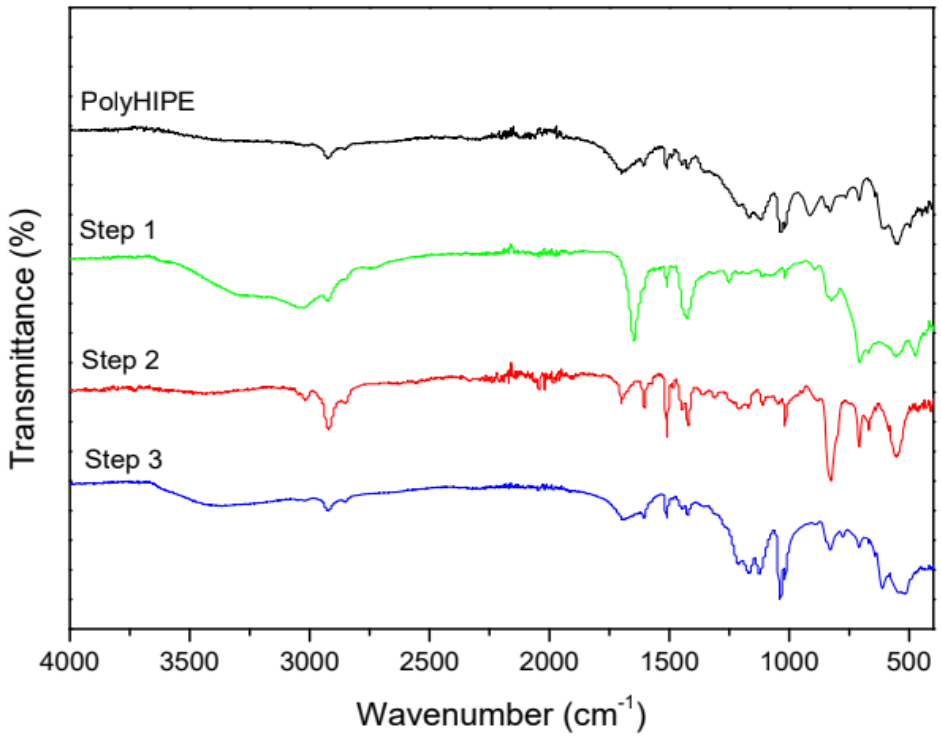

Figure 4.10 : FT-IR graphs of PolyHIPE (PHP) and the modification steps.

The peak at 1485 cm^{-1} observed for all kind of polymers is the characteristic of the aromatic ring originated from the polyHIPE containing VBC and DVB. The reaction with thiourea in EtOH introduces benzyl thiouronium salt which can be proved by disappearing C−Cl stretching vibration at 685 cm^{-1} and new absorption band at 1641 cm^{-1} (C=N strecthing) and very broad band around 3200 cm^{-1} (N-H stretching) in Figure 4.10 (Step 1). The hydrolysis of thiouronium salt on polyHIPE surface was successfully accomplished based on disappearing the characteristic absorption bands of thiouronium salts (Step 2 in Figure 4.10). And finally, the oxidation with H_2O_2 produced $–SO_3H$ group which was confirmed by O=S=O stretching vibrations at 1045 cm^{-1} and a broad absorption band of O-H stretching at 3100-3700 cm^{-1} (Step 3 in Figure 4.10). FT-IR analysis was also performed to charaterize the HXL-PHPs prepared by the hypercrosslinking reaction for 15 min. In Figure 4.11, it can be observed that C−Cl stretching vibration (685 cm^{-1}) and phenyl chloride (1260 cm^{-1}) peaks, related to VBC pendant groups, decreased after the Friedel−Crafts reaction confirming the successful hypercrosslinking reaction. The oxidation with H_2O_2 produced $–SO_3H$ group which was confirmed by O=S=O stretching vibrations at 1045 cm^{-1} and a broad absorption band of O-H stretching at 3100-3700 cm^{-1} (Figure 4.11).

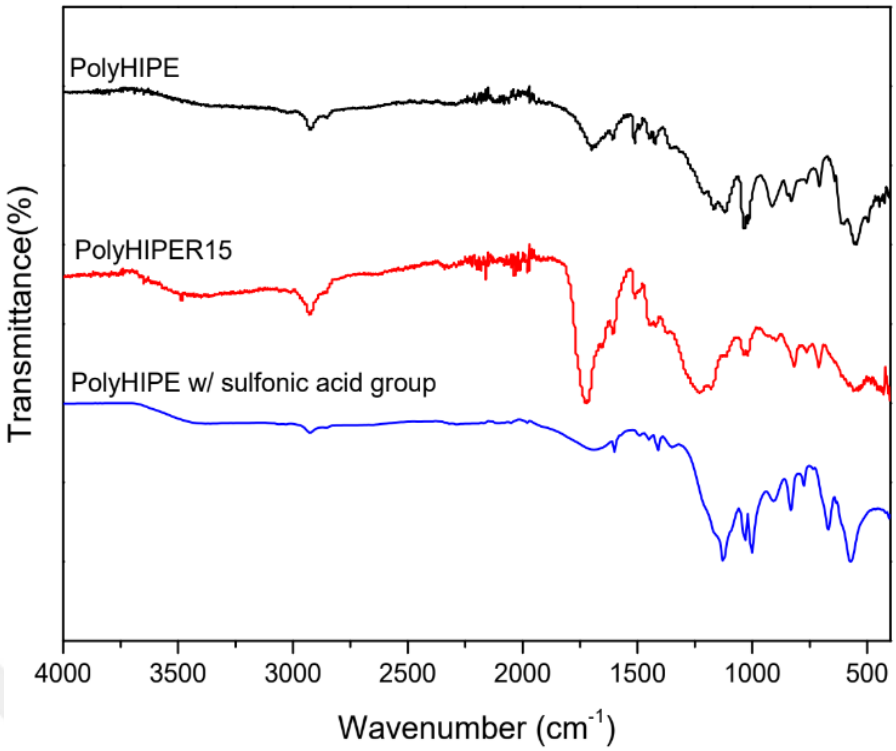

Figure 4.11 : FT-IR graphs of PolyHIPE, HXL-15min-and the modification steps.

To obtain a solid acid catalyst with high surface area, the hypercrosslinking reaction was studied kinetically to determine the unracted chlorine groups for furher functionalization reactions. The chlorine content of the polyHIPE catalysts was measured by mercury(II) thiocynate method. The method is based on the displacement of thiocyanate ion from mercury(II) thiocyanate by chloride ion. When iron(III) ion is present in the environment, a highly coloured iron(III) thiocyanate complex is formed. The intensity of its colour is proportional to the original chloride ion concentration:

$$2Cl^- + Hg(SCN)_2 + 2Fe^{+3} \rightarrow HgCl_2 + 2[Fe(SCN)]^{2+} \quad (4.1)$$

To determine the chlorine content of polyHIPEs, 200 mg polyHIPE was placed in a 100 mL round bottom flask and 20 ml NaOH/EtOH (10%, w/v) solution containing 1 mL distilled water was added into this flask. The mixture was heated at reflux temperature for 2 h. And then the mixture was cooled down to room temperature and filtered under gravity. 10 mL aliquot of the chloride solution in a 25 mL was placed in a graduated flask and 2.0 mL of 0.25M ammonium iron(III) sulphate $[Fe(NH_4)(SO_4)_2,12H_2O]$ in 9M nitric acid was added into the flask followed by addition 2.0 mL of a saturated solution of mercury(II) thiocyanate in ethanol. After 10 min, the absorbance of the sample solution and also of the blank was measured by UV

spectrophotometer at 460 nm. The amount of chloride ion in the sample corresponds to the difference between the two absorbances and is obtained from a calibration curve. The calibration curve was constructed by using a standard sodium chloride solution containing 10 μg Cl^- / mL covering the range 0-50 μg (Figure 4.12).

According to the calculations based on the chlorine determination, VBC polyHIPE prcursor has 5.8 mmol/g chlorine content and HXL-15min-PHP has 3.4 mmol/g chlorine content. These results are in a good agreement with sulfonic acid content determination results which prove high conversions. The sulfonic acid group contents of solid acid catalysts were determined by acid-base back titration. Acording to the results, PHP-SO_3H has 4.2 mmol/g sulfonic acid capacity and HXL-PHP-SO_3H has 2.0 mmol/g sulfonic acid capacity.

PolyHIPEs have low surface area because of large pores (voids and windows). It was expected that hypercrosslinking reaction change the pore structure of polyHIPEs by intruducing micro- and mesopores. These new pores also are expected to increse the surface area of the polyHIPE. The meso/micro porosity of the materials was analyzed with the Brunauer−Emmett−Teller (BET) isotherm model. It is a fact that the unreacted benzyl chloride groups are necassry to introduce sulfonic acid groups to the polymer surface, hypercrosslinking reaction was limited to 15 minutes. N_2 adsorption isotherms of polyHIPE and HXL-PHPs can be seen in Figure 4.13. Additionally, BET surface areas (S_{BET}), pore volume (V_p), average pore size and micropore volume are given in Table 4.1.

It can be observed from the data in Table 4.1 that the low surface area (S_{BET} = 10.46 m^2/g) was obtained for polyHIPE precursor (PHP) due to its macroporous structure possessing large voids and windows. However, just 15 min hypercrosslinking reaction increased the surface area of polyHIPE to 257.1 m^2/g.

The effect of hypercrosslinking reaction on pore size and pore size distribution was investigated. The pore size distribution from the BJH method shows that hypercrosslinking reaction caused a significant increase in mesoporosity (Figure 4.14). Furthermore, the pore volume was increased more than 10-fold only in 15 minutes by hypercrosslinking reaction.

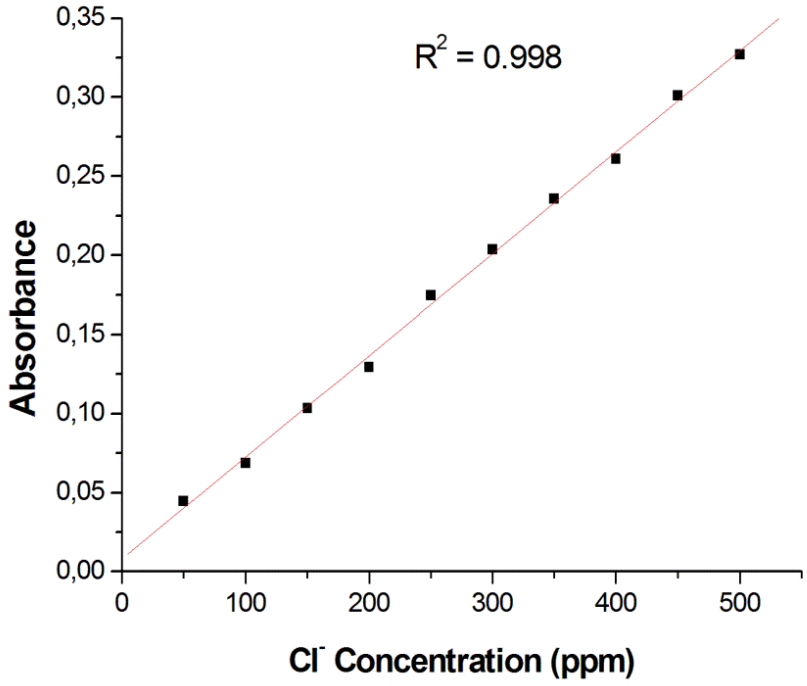

Figure 4.12 : Calibration curve for chlorine content.

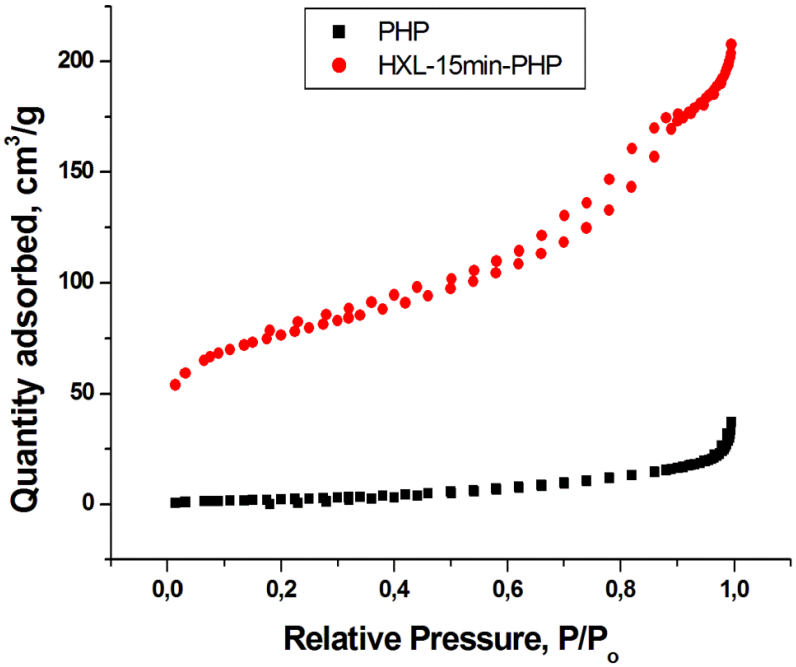

Figure 4.13 : Nitrogen adsorption-desorption isotherms.

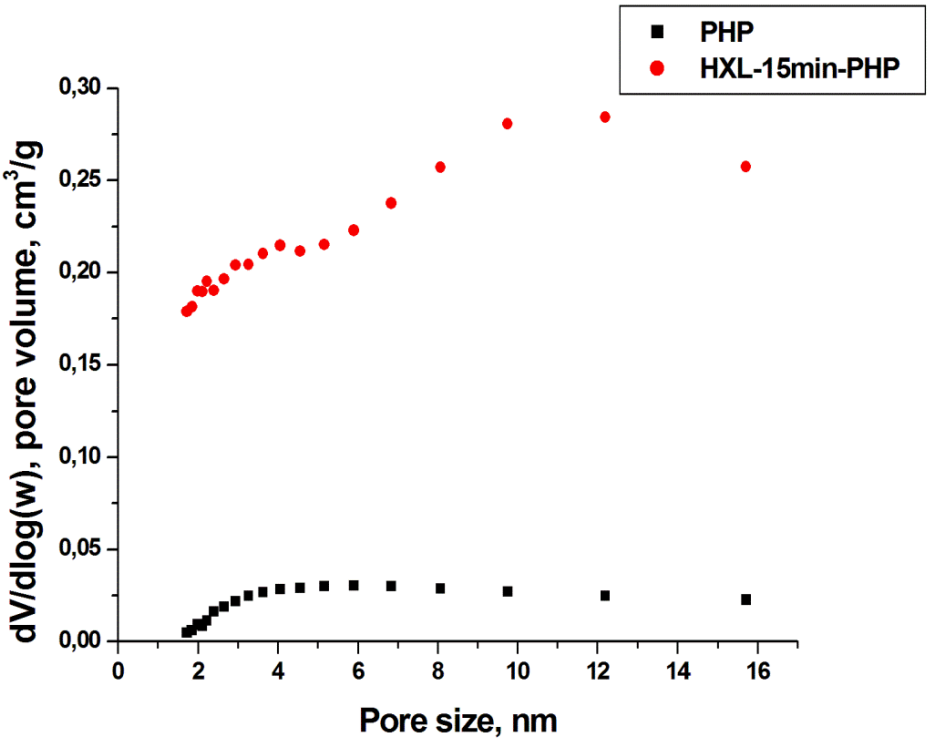

Figure 4.14 : Pore size distribution for PHP and HXL-15min-PHP.

4.4 Esterification Reactions (Catalyst Testing)

In this thesis, porous polymers were prepared by emulsion-template method as polymer supports for solid acid catalysts. These heterogeneous catalysts were successfully used to catalyze the esterification reaction between oleic acid and methanol for biodiesel production.

Recently waste cooking oils (WCOs) have been started to be used for biodiesel production to lower the cost of feedstock [3]. For this reaction, generally basic catalysts are used due to their enhanced reaction rate. However, high content of Free fatty acids in WCOs can show the poisonous effect and deactivate the basic catalysts used for transesterification to produce biodiesel. Therefore, the esterification catalyzed by acid catalysts as a pre-treatment to reduce acid value for WCOs is necessary. The porous polymers prepared in this thesis can be used in this pre-treatment process for a more efficient biodiesel production. Compared to basic catalysts, acid catalysts are not affected by FFAs. However, conventional homogeneous acid catalysts have some disadvantages such as corrosion of equipment and large amount of waste for purification which contribute to environmental pollution. Heterogeneous catalyst can be used many times without creating additional pollution. Moreover, the simultaneous

esterification and transesterification (SET) catalyzed by solid heterogeneous catalysts has been shown to be the most economic method [49]. Therefore, the solid acids have a potential as efficient catalysts for biodiesel production.

The solid acids show hydrophilicity due to the polar acidic sites on their surface. Water is a common solvent and also a byproduct in many acid-catalyzed reactions. It can be adsorbed on the surface of acidic catalysts and poison the catalytic site. The new solid acid catalysts with some degree of hydrophobicity can overcome these drawbacks and enhances their catalytic activities and reusability.

Because the raw materials (animal fats, vegetable seed oil, soybean oil etc.) contain molecules having unsaturated bonds it makes the obtained biodiesel more susceptible to the oxidative processes [50]. The oxidative reactions generate free radicals which can cause leaching of active groups of solid catalysts.

The solid catalyst prepared by the emulsion-templated method in this thesis has three advantages:

i. The higher surface area obtained by additional meso- and micropores.
ii. A controlled hydrophobicity through multi-step modification resulting sulfonic acid groups.
iii. The sulfonic acid groups connected to the benzene ring with a methylene spacer group which prevent leaching of sulfonic acid groups by radicals [51]. The following catalysts testing experiments were carried out to prove the mentioned advantageous of the catalyst.

First, a solid catalyst was prepared by using VBC and DVB as crosslinker and benzyl chloride groups were converted to sulfonic acid groups. This solid catalyst was tested in the esterification reaction between oleic acid and methanol (Figure 4.15).

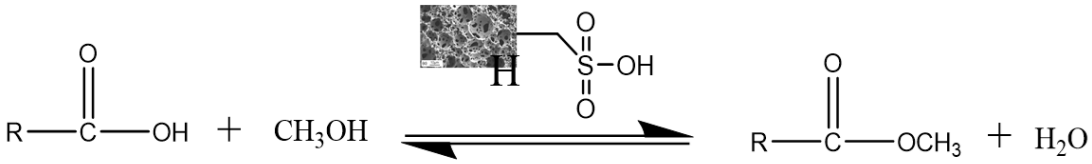

Figure 4.15 : Esterification reaction between oleic acid methanol.

The effect of the catalyst amount on the esterification was studied and the results can be observed in Table 4.2. It can be seen that the non-catalyzed esterification is very slow while polyHIPE based solid catalyst prompted the esterification of oleic acid with

methanol significantly. The catalytic efficiency for acid reduction via esterification could be obtained by 77.5% with the catalysts amount of 10 mol% based on the mol number of oleic acid for the reaction time of 3 hours at 90°C. Because the further increase in the catalyst amount did not change the catalytic performance (20% mol catalyst) 10% was applied to the further catalytic experiments in this thesis.

Table 4.2 : The effect of catalyst amount on catalytic performance of polyHIPE catalyst[3]

Catalyst amount, mol%[4]	Catalytic efficiency (η%)
0	8.05
5	59.6
10	77.5
20	79.0

The reaction between oleic acid and methanol is reversible. The molar ratio of methanol to oleic acid needs to be bigger than the theoretical value of 1 to enhance the forward reaction. Therefore, the effect of the molar ratio of methanol to oleic acid on the esterification catalyzed by PHP-SO_3H was also studied. As can be seen in Figure 4.16, as the molar ratio of methanol to oleic acid increases from 3 to 8, the esterification efficiency was obtained from 42.14% to 68.37 % at 90°C. Moreover, when the ratio was used more than 8, the reaction efficiency was observed as remaining the same value. Although high methanol to oleic acid molar ratios are necassary for high catalytic efficiencies, extreme amount of ethanol can dilute the reaction enviroment leading to the slower reaction rates.

Because this thesis aims to compare low- and high-surface-area polyHIPE-based acid catalysts, the esterification reactions were carried out at various time intervals with using both PHP-SO_3H and HXL-15min-PHP-SO_3H. As can be clearly seen in Figure 4.17 that HXL-PHP carrying sulfonic acid groups enhanced the reactions kinetics compared to the unhypercrosslinked counterpart. The high surface area obtained by mezo- and micropores allow the reactants to reach surface active groups in a faster way leading high efficiencies in a shorter period of time.

[3] Experimental conditions: molar ratio of oleic acid to methanol = 8; Reaction temperature = 90°C
[4] Based on the mol number of oleic acid

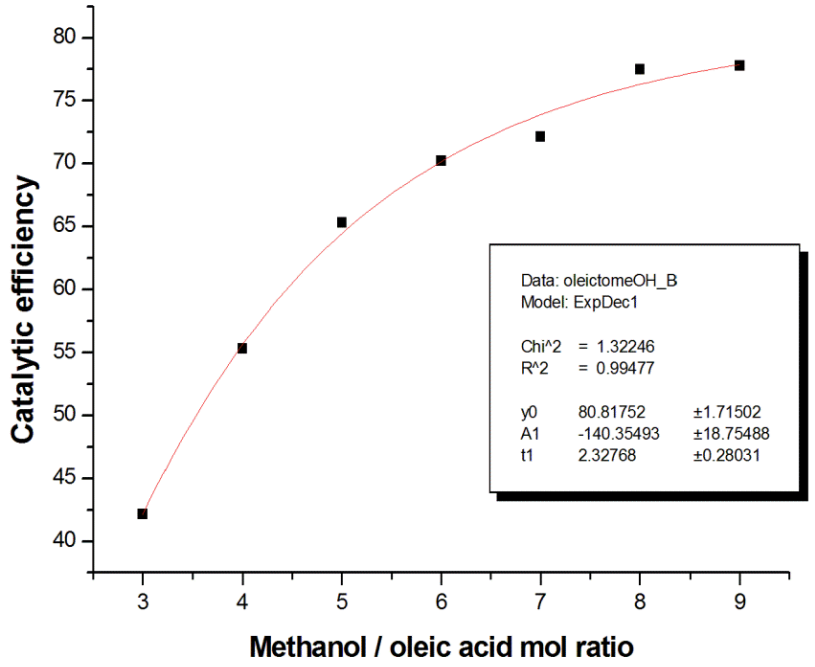

Figure 4.16 : Catalytic efficiency according to the molar ratio of methanol to oleic acid.

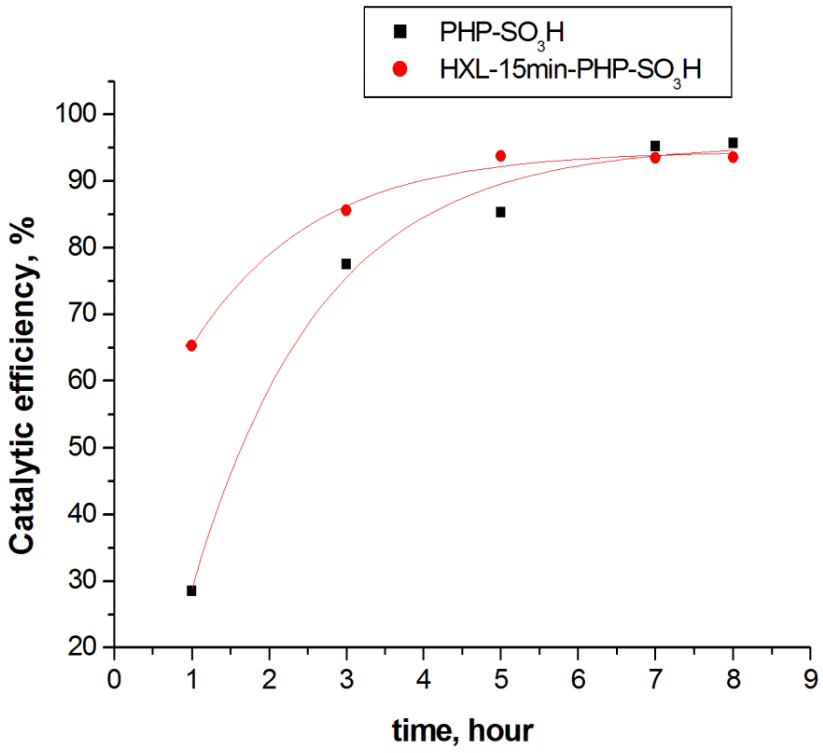

Figure 4.17 : Kinetic performance comparison for PHP-SO_3H and HXL-15min-PHP-SO_3H

The last effect on the catalytic reaction examined in this thesis was temperature. Because the esterification reaction is endothermic the reaction temperature should shift the equilibrium towards the production side. Moreover, at higher reaction temperatures, reactants can reach to the surface-active sites more easily. As can be observed in Figure 4.18 as the reaction temperature increases from 25°C to 100°C, the efficiency increases from 32.2% to 76.5%.

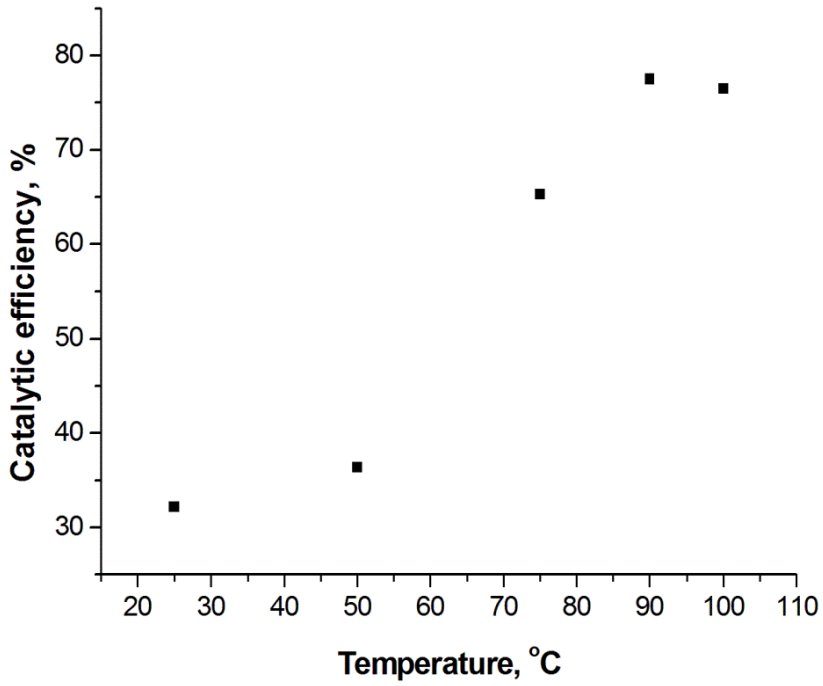

Figure 4.18 : Catalytic efficiency according to reaction temperature in esterification.

4.5 The Recyclability and Stability of the Solid Catalysts

One main advantage of heterogeneous catalysts is their re-use ability due to crosslinked nature of the structure. To prove that the polyHIPE based catalyst can be used many times in multiple cycles, the additional catalytic runs were carried out. The solid catalyst was isolated from the reaction medium through filtration under vacuum followed by washing with excess methanol to regenerate the active sites. This procedure was applied to both the sulfonic acid catalyst with methylene bridge and the one which was obtained by sulfonation. Water is a by-product of esterification reaction. The produced water can lead the reversible reaction towards reactant-side and deactivate the solid catalyst. Therefore, we compare the efficiency of the both catalyst in multiple catalytic cycles. As can be seen in Figure 4.19 that polyHIPE

catalysts with sulfonic acid active groups obtained in a controlled way had better stability and recyclability compared to the one which was obtained by direct sulfonation.

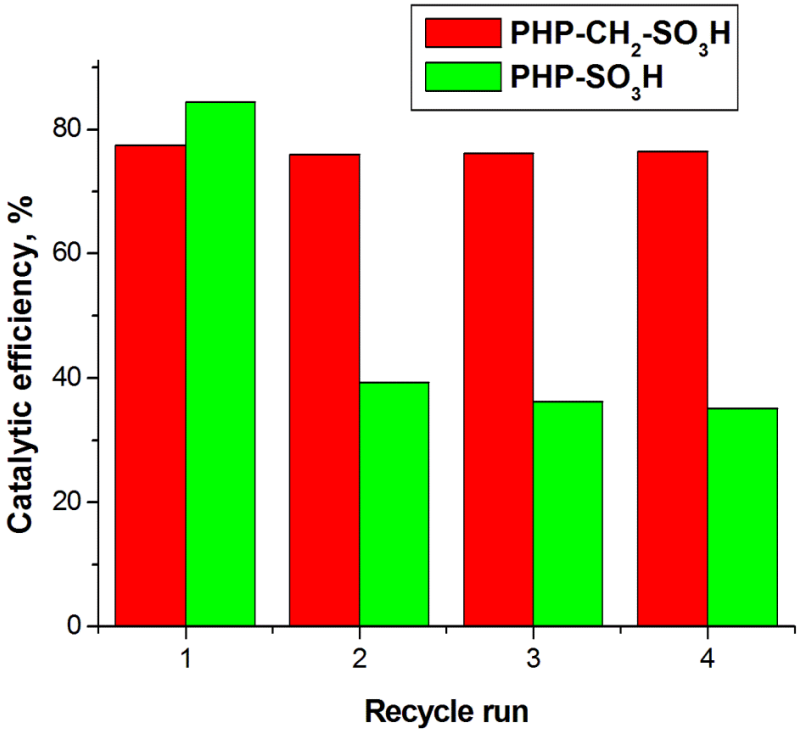

Figure 4.19 : Catalyst recycling results of the polyHIPE catalysts.

5. CONCLUSION

In this thesis polymeric solid catalysts were prepared for the esterification reaction between methanol and oleic acid. The emulsion template method was used to prepare these polymers known as polyHIPE. The polymers were characterized by SEM, FT-IR, BET nitrogen adsorption and analytical methods. The SEM images showed that all catalysts prepared in this thesis have interconnected, open-porous structure. Originally polyHIPEs have low surface area due to the large pores in their structure. Therefore, the hypercrosslinking reaction was applied to increase the surface area of polyHIPEs. As the BET results prove the HXL-PHPs have significant increase in their surface area. The polyHIPE surface was tailored with sulfonic acid groups via multi-step protocol which enabled to attach the sulfonic acid groups to the polymer through a methylene bridge. This methylene bridge prevents the leaching of sulfonic acid groups by radicals produced during biodiesl production. Moreover, by this strategy, it is possible to control the amount of sulfonic acid groups and the hydrophobicity of polymer surface. The ability of controlling surface hydrophobicity is essential for solid catalysts. To prove the advantage of the polyHIPE catalyst with methylene bridge, additional polyHIPE was prepared and sulfonated by chlorosulfonic acid resulting surface sulfonic acid groups directly attached to the polymer. The recycle catalytic runs showed clearly that polyHIPE solid catalyst did not lose the catalytic ability after four cycles while the additional polyHIPE lost its more than half catalytic capacity even after second run.

REFERENCES

[1] **Maheshwari, P., Haider, M. B., Yusuf, M., Klemeš, J. J., Bokhari, A., Beg, M., Al-Othman, A., Kumar, R., & Jaiswal, A. K.** (2022). A review on latest trends in cleaner biodiesel production: Role of feedstock, production methods, and catalysts. *Journal of Cleaner Production*, 355, 131588. https://doi.org/10.1016/j.jclepro.2022.131588

[2] **Cameron, N. R., & Sherrington, D. C.** (1996). High internal phase emulsions (HIPEs)—Structure, properties and use in polymer preparation. *In Biopolymers Liquid Crystalline Polymers Phase Emulsion* (pp. 163–214). Springer. https://doi.org/10.1007/3-540-60484-7_4

[3] **Atadashi, I. M., Aroua, M. K., Abdul Aziz, A. R., & Sulaiman, N. M. N.** (2013). The effects of catalysts in biodiesel production: A review. *Journal of Industrial and Engineering Chemistry*, 19(1), 14–26. https://doi.org/10.1016/j.jiec.2012.07.009

[4] **Dizge, N., Keskinler, B., & Tanriseven, A.** (2009). Biodiesel production from canola oil by using lipase immobilized onto hydrophobic microporous styrene–divinylbenzene copolymer. *Biochemical Engineering Journal*, 44(2), 220–225. https://doi.org/10.1016/j.bej.2008.12.008

[5] **Babadi, A. A., Rahmati, S., Fakhlaei, R., Barati, B., Wang, S., Doherty, W., & Ostrikov, K. (Ken).** (2022). Emerging technologies for biodiesel production: Processes, challenges, and opportunities. *Biomass and Bioenergy*, 163, 106521. https://doi.org/10.1016/j.biombioe.2022.106521

[6] **Atadashi, I. M., Aroua, M. K., Abdul Aziz, A. R., & Sulaiman, N. M. N.** (2012). Production of biodiesel using high free fatty acid feedstocks. *Renewable and Sustainable Energy Reviews*, 16(5), 3275–3285. https://doi.org/10.1016/j.rser.2012.02.063

[7] **Thangaraj, B., Solomon, P. R., Muniyandi, B., Ranganathan, S., & Lin, L.** (2019). Catalysis in biodiesel production—A review. *Clean Energy*, 3(1), 2–23. https://doi.org/10.1093/ce/zky020

[8] **Şenol, N.** (2010). *Catalyst Development for Hydrogen Production From Natural Gas* [M.Sc., Ankara University]. https://tez.yok.gov.tr/UlusalTezMerkezi/TezGoster?key=zqI_ZOq-b18GC2rT9c2JGuJLr17wwJLzSyo8UxSyoGu6HG-VD6PH57JM7eoJJbIP

[9] **Kozuch, S., & Martin, J. M. L.** (2012). "Turning Over" Definitions in Catalytic Cycles. *ACS Catalysis*, 2(12), 2787–2794. https://doi.org/10.1021/cs3005264

[10] **Avşar, G.** (2008). *Synthesis of Novel Fluorinated Phosphine and Their Rhodium(I) Complexes and Application of Hydrogenation Reactions in Supercritical Carbon Dioxide* [Ph.D., Çukurova University]. https://tez.yok.gov.tr/UlusalTezMerkezi/TezGoster?key=biL2P3cCsPgUNjVdV2BsGMeCFeixAhsEjZqY5NB3t8_ZBb2G5GXFwN5JwU68EoSt

[11] **Ruhul, A. M., Kalam, M. A., Masjuki, H. H., Fattah, I. M. R., Reham, S. S., & Rashed, M. M.** (2015). State of the art of biodiesel production processes: A review of the heterogeneous catalyst. *RSC Advances*, 5(122), 101023–101044. https://doi.org/10.1039/C5RA09862A

[12] **Mazi, H., & Esen, Y.** (2021). New, Effective and Reusable Polymeric Heterogeneous Catalysts for Poly(urethane) Production. *Catalysis Surveys from Asia*, 25(1), 93–100. https://doi.org/10.1007/s10563-020-09316-2

[13] **Sharma, Y. C., Singh, B., & Korstad, J.** (2011). Latest developments on application of heterogenous basic catalysts for an efficient and eco friendly synthesis of biodiesel: A review. *Fuel*, 90(4), 1309–1324. https://doi.org/10.1016/j.fuel.2010.10.015

[14] **Agarwal, M., Singh, K., & Chaurasia, S. P.** (2012). Kinetic modeling for biodiesel production by heterogeneous catalysis. *Journal of Renewable and Sustainable Energy*, 4(1), 013117. https://doi.org/10.1063/1.3687941

[15] **Andrijanto, E.** (2012). *The study of heterogeneous catalysts for biodiesel synthesis* [Ph.D., University of Huddersfield]. https://www.proquest.com/docview/1651907290/F571F08E69074299PQ/2

[16] **Koler, A., Pulko, I., & Krajnc, P.** (2020). Post Polymerisation Hypercrosslinking with Emulsion Templating for Hierarchical and Multi-Level Porous Polymers. *Acta Chimica Slovenica*, 67(2), 349–360. https://doi.org/10.17344/acsi.2020.5901

[17] **Sun, Q., Dai, Z., Meng, X., & Xiao, F.-S.** (2015). Porous polymer catalysts with hierarchical structures. *Chemical Society Reviews*, 44(17), 6018–6034. https://doi.org/10.1039/C5CS00198F

[18] **Mert, H. H., Mert, M. S., & Mert, E. H.** (2019). A statistical approach for tailoring the morphological and mechanical properties of polystyrene PolyHIPEs: Looking through experimental design. *Materials Research Express*, 6(11), 115306. https://doi.org/10.1088/2053-1591/ab437f

[19] **Yang, X.-Y., Chen, L.-H., Li, Y., Rooke, J. C., Sanchez, C., & Su, B.-L.** (2017). Hierarchically porous materials: Synthesis strategies and structure design. *Chemical Society Reviews*, 46(2), 481–558. https://doi.org/10.1039/C6CS00829A

[20] **Foudazi, R.** (2021). HIPEs to PolyHIPEs. *Reactive and Functional Polymers*, 164, 104917. https://doi.org/10.1016/j.reactfunctpolym.2021.104917

[21] **Cameron, N. R., Krajnc, P., & Silverstein, M. S.** (2011). Colloidal Templating. In Porous Polymers (pp. 119–172). *John Wiley & Sons, Ltd.* https://doi.org/10.1002/9780470929445.ch4

[22] **Thumbarathy, D.** (2018). *A Preparation of functional polyHIPE polymers for agro-process and bio-process applications* [Thesis, Newcastle University]. http://theses.ncl.ac.uk/jspui/handle/10443/4049

[23] **Mert, E. H.** (2010). *Synthesis, modification and characterisation of polyester based cross-linked, porous polyHIPE materials* [Ph.D., Yıldız Technical University]. YÖKTEZ. https://tez.yok.gov.tr/UlusalTezMerkezi/TezGoster?key=zqI_ZOq-b18GC2rT9c2JGseJ9aDDRPEuCF6yHCo2uW_LQ7Eyxsl1zpwW4cxOxuIu

[24] **Hiemenz, P. C., & Rajagopalan, R.** (1997). Principles of Colloid and Surface Chemistry, Revised and Expanded. *CRC Press*.

[25] **Zhao, B.** (2019). *Polyhipes Morphology, Surface Modification and Transport Properties* [Ph.D.]. https://www.proquest.com/docview/2515027360/abstract/5D2ACDEA59664A5BPQ/1

[26] **Yavuz, E., Cherkasov, N., & Degirmenci, V.** (2019). Acid and base catalysed reactions in one pot with site-isolated polyHIPE catalysts. *RSC Advances*, 9(15), 8175–8183. https://doi.org/10.1039/C9RA01053J

[27] **Öngül, H. B.** (2019). *PolyHIPE Supported Sorbent for Selective Mercury Removal From Aqueous Solutions* [M.Sc., İstanbul Technical University]. https://tez.yok.gov.tr/UlusalTezMerkezi/TezGoster?key=Mir2lXQK1dkmQ9Ige3PZbgltfsKrv7kXyQ5pM80wigih8g8IzLCFjeoFAeGhJnUn

[28] **Fontanals, N., M. Marcé, R., Borrull, F., & G. Cormack, P. A.** (2015). Hypercrosslinked materials: Preparation, characterisation and applications. *Polymer Chemistry*, 6(41), 7231–7244. https://doi.org/10.1039/C5PY00771B

[29] **Huang, J., & Turner, S. R.** (2018). Hypercrosslinked Polymers: A Review. *Polymer Reviews*, 58(1), 1–41. https://doi.org/10.1080/15583724.2017.1344703

[30] **Barkan-Öztürk, H., Menner, A., Bismarck, A., & Woodward, R. T.** (2022). Simultaneous hypercrosslinking and functionalization of polyHIPEs for use as coarse powder catalyst supports. *Chemical Engineering Science*, 264, 118151. https://doi.org/10.1016/j.ces.2022.118151

[31] **Gokmen, M. T., & Du Prez, F. E.** (2012). Porous polymer particles—A comprehensive guide to synthesis, characterization, functionalization and applications. *Progress in Polymer Science*, 37(3), 365–405. https://doi.org/10.1016/j.progpolymsci.2011.07.006

[32] **Hoşgün, S.** (2018). *Synthesis and Characterization of Cobalt and Nickel Based Catalysts and Their Use in Hydrogen Production by the Hydrolysis Reaction of Sodium Borohydride* [Ph.D., Eskişehir Osmangazi University]. https://tez.yok.gov.tr/UlusalTezMerkezi/TezGoster?key=T1mWGp9MngYYkCSgiJvtVsvdsbnqIz-cMZNPbp3QnONay9valooVrxIeFNoNZd_S

[33] **Haber, J., Block, J. H., & Delmon, B.** (2008). Methods and Procedures for Catalyst Characterization. In Handbook of Heterogeneous Catalysis (pp. 1230–1258). *John Wiley & Sons, Ltd.* https://doi.org/10.1002/9783527610044.hetcat0066

[34] **Silverstein, M. S.** (2014). PolyHIPEs: Recent advances in emulsion-templated porous polymers. *Progress in Polymer Science*, 39(1), 199–234. https://doi.org/10.1016/j.progpolymsci.2013.07.003

[35] **Zhu, J., Wu, L., Bu, Z., Jie, S., & Li, B.-G.** (2019). Polyethylenimine-Grafted HKUST-Type MOF/PolyHIPE Porous Composites (PEI@PGD-H) as Highly Efficient CO_2 Adsorbents. *Industrial & Engineering Chemistry Research*, 58(10), 4257–4266. https://doi.org/10.1021/acs.iecr.9b00213

[36] **Aldemir Dikici, B., Malayeri, A., Sherborne, C., Dikici, S., Paterson, T., Dew, L., Hatton, P., Ortega Asencio, I., MacNeil, S., Langford, C.,**

Cameron, N. R., & Claeyssens, F. (2022). Thiolene- and Polycaprolactone Methacrylate-Based Polymerized High Internal Phase Emulsion (PolyHIPE) Scaffolds for Tissue Engineering. *Biomacromolecules*, 23(3), 720–730. https://doi.org/10.1021/acs.biomac.1c01129

[37] **Zhang, Y., Chen, Y., Shen, Y., Yan, Y., Pan, J., Shi, W., & Yu, L.** (2016). Hierarchically Macro-/Mesoporous Polymer Foam as an Enhanced and Recyclable Catalyst System for the Sustainable Synthesis of 5-Hydroxymethylfurfural from Renewable Carbohydrates. *ChemPlusChem*, 81(1), 108–118. https://doi.org/10.1002/cplu.201500357

[38] **Takagaki, A., Ohara, M., Nishimura, S., & Ebitani, K.** (2009). A one-pot reaction for biorefinery: Combination of solid acid and base catalysts for direct production of 5-hydroxymethylfurfural from saccharides. *Chemical Communications*, 41, 6276–6278. https://doi.org/10.1039/B914087E

[39] **Üzüm, G., Akın Özmen, B., Tekneci Akgül, E., & Yavuz, E.** (2022). Emulsion-Templated Porous Polymers for Efficient Dye Removal. *ACS Omega*, 7(18), 16127–16140. https://doi.org/10.1021/acsomega.2c01472

[40] **Dizge, N., Aydiner, C., Imer, D. Y., Bayramoglu, M., Tanriseven, A., & Keskinler, B.** (2009). Biodiesel production from sunflower, soybean, and waste cooking oils by transesterification using lipase immobilized onto a novel microporous polymer. *Bioresource Technology*, 100(6), 1983–1991. https://doi.org/10.1016/j.biortech.2008.10.008

[41] **Vogel, A. I., Jeffery, G. H., & Vogel, A. I.** (1978). Vogel's textbook of quantitative chemical analysis (4th ed). *Longman Scientific & Technical ; Wiley.*

[42] **Zhou, Y., Niu, S., & Li, J.** (2016). Activity of the carbon-based heterogeneous acid catalyst derived from bamboo in esterification of oleic acid with ethanol. *Energy Conversion and Management*, 114, 188–196. https://doi.org/10.1016/j.enconman.2016.02.027

[43] **Liu, F., Huang, K., Zheng, A., Xiao, F.-S., & Dai, S.** (2018). Hydrophobic Solid Acids and Their Catalytic Applications in Green and Sustainable Chemistry. *ACS Catalysis*, 8(1), 372–391. https://doi.org/10.1021/acscatal.7b03369

[44] **Cameron, N. R.** (2005). High internal phase emulsion templating as a route to well-defined porous polymers. *Polymer*, 46(5), 1439–1449. https://doi.org/10.1016/j.polymer.2004.11.097

[45] **Pulko, I., & Krajnc, P.** (2012). High Internal Phase Emulsion Templating – A Path to Hierarchically Porous Functional Polymers. *Macromolecular Rapid Communications*, 33(20), 1731–1746. https://doi.org/10.1002/marc.201200393

[46] **Barbetta, A., & Cameron, N. R.** (2004). Morphology and Surface Area of Emulsion-Derived (PolyHIPE) Solid Foams Prepared with Oil-Phase Soluble Porogenic Solvents: Span 80 as Surfactant. *Macromolecules*, 37(9), 3188–3201. https://doi.org/10.1021/ma0359436

[47] **AlMarzooqi, F. A., Bilad, M. R., Mansoor, B., & Arafat, H. A.** (2016). A comparative study of image analysis and porometry techniques for characterization of porous membranes. *Journal of Materials Science*, 51(4), 2017–2032. https://doi.org/10.1007/s10853-015-9512-0

[48] **Yang, X., Tan, L., Xia, L., Wood, C. D., & Tan, B.** (2015). Hierarchical Porous Polystyrene Monoliths from PolyHIPE. *Macromolecular Rapid Communications*, 36(17), 1553–1558. https://doi.org/10.1002/marc.201500235

[49] **Jacobson, K., Gopinath, R., Meher, L. C., & Dalai, A. K.** (2008). Solid acid catalyzed biodiesel production from waste cooking oil. *Applied Catalysis B: Environmental*, 85(1), 86–91. https://doi.org/10.1016/j.apcatb.2008.07.005

[50] **Yaakob, Z., Narayanan, B. N., Padikkaparambil, S., Unni K., S., & Akbar P., M.** (2014). A review on the oxidation stability of biodiesel. *Renewable and Sustainable Energy Reviews*, 35, 136–153. https://doi.org/10.1016/j.rser.2014.03.055

[51] **Fei, G., Shin, J., Kang, S.-A., Ko, B.-S., Kang, P.-H., Lee, Y.-S., & Nho, Y. C.** (2010). Preparation and characterization of a poly(vinylbenzyl sulfonic acid)-grafted FEP membrane. *Journal of Polymer Science Part A: Polymer Chemistry*, 48(3), 563–569. https://doi.org/10.1002/pola.23762

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