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Synthesis of mesoporous silica-carbon composite as solid acid catalyst for esterification reaction

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ABSTRACT

Background: In industrial process, there are numerous of reactions that need catalyst to be involved with, the typical catalyst used is of homogenous catalyst, that in fact, having several adversities in the process. Apparently, the homogenous catalyst may contain high toxicity, causing corrosion, and the difficulty of separating catalyst from the product resulted in the end of the process.. **Methods:** The purpose of this research are to evaluate the performance of solid acid catalysts with PEG template in the esterification reaction and determine the effect of sulfonation temperature on the characteristics of the catalyst. **Findings:**The synthesis procedure of a solid acid catalyst with PEG templates includes the synthesis of silica gel, carbonization, sulfonation, product characterization and esterification. Making silica gel using PEG as a carbon source and template was made by preparing a solution of waterglass (Na_2SiO_3) with a concentration of 8% SiO2. Besides that, a solution of 1 M hydrochloric acid (HCl) and 1 M sodium hydroxide (NaOH) solution were prepared. The template is removed by calcination at a temperature of 550ºC for 1 hour. Sulfonation was carried out by mixing silica-carbon composites with a concentrated 98% H_2SO_4 solution and heated at temperature variables (80^0C, 120^0C, 100^0C, 135^0C, and 150^0C). While esterification was carried out with a variation of the catalyst mass of 0.2, 0.5, and 0.8 grams on the best results carried out at temperatures of 60^0C, 70^0C, and 80^0C. The sample is characterized with Nitrogen Adsorption/Desorption Isotherms, Scanning Electron Microscopy (SEM), and Energy Dispersive X-Ray Analysis (EDAX), Spectrophotometry FTIR (Fourier Transform Infra Red), ionic capacity experiment, and esterification reaction experiment. **Conclusion:** The study confirms that sulfonation temperature significantly influences the catalytic performance of PEG-templated silica-carbon solid acid catalysts in esterification reactions. **Novelty/Originality of this Article**: This research introduces a PEG-templated silica-carbon composite as a solid acid catalyst with tunable sulfonation temperatures to enhance esterification efficiency.

KEYWORDS: acid catalyst; esterification; PEG; silica-carbon composite.

1. Introduction

Currently, most chemical industries use solid catalysts in their production processes, including industries such as lubricating oil, Medco, Pertamina, as well as in biodiesel production processes. Biodiesel fuel can be produced through one of two methods: either by transesterifying vegetable oils with alcohol or by direct esterification of fatty acids with alcohol and a homogeneous acid catalyst (Marchetti et al., 2011). The use of homogeneous catalysts in esterification reactions has some drawbacks. Homogeneous catalysts are considered less advantageous because they are highly toxic, cause corrosion, and are difficult to separate from the final product. These difficulties arise because special methods

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are required for separation, which reduces production efficiency. Moreover, homogeneous catalysts are typically prone to decomposition at temperatures above 100°C. Therefore, there is a need to develop solid acid catalysts that can be easily separated from the product (Prasetyo et al., 2014).

A catalyst serves to lower the activation energy of a reaction, allowing the reaction to occur more quickly. In practical applications, heterogeneous catalysts are considered superior because they are easier to separate. However, in reality, catalysts commonly used in esterification reactions are typically liquid-phase (homogeneous) catalysts. Catalysts can be either basic or acidic. In practice, basic catalysts have the advantage of increasing reaction speed more effectively than acidic catalysts. However, basic catalysts have the drawback of producing less ester product compared to acidic catalysts. Additionally, the use of basic catalysts in transesterification reactions can lead to a side reaction, saponification, which complicates the separation of the final products. Acidic catalysts commonly used in esterification reactions include hydrochloric acid, sulfuric acid, or sulfonic acid. Given the relative ineffectiveness of basic catalysts compared to acidic ones, acid catalysts were selected for this research.

The expected outcome of this research is the development of a solid acid catalyst made from a silica-carbon composite. The desired properties of the catalyst are high reactivity, environmental friendliness, short reaction time, and ease of handling at low cost (Shaterian et al., 2008). Previous research on silica has been extensive due to its unique properties. Silica is a chemical compound with the molecular formula SiO_2, which can be obtained from plant-derived silica, minerals, and crystal synthesis. Silica has a large surface area and volume with an organized pore structure. It is stable, cost-effective, and has organic groups that easily access the surface to provide catalytic centers (Gupta et al., 2008). Furthermore, silica is a compound with silanol groups on its surface, providing sites for other compounds to be grafted (Chavan et al., 2008).

Several studies have been developed to produce catalysts with a large surface area, particularly for making solid acid catalysts. Solid acid catalysts are considered more effective in esterification reactions from an economic standpoint, as they reduce downstream processing needed for separating products and catalysts without the occurrence of saponification reactions (Zhang et al., 2003). Various methods have been developed to create solid acid catalysts with large surface areas. One of these methods is the sol-gel process. Several solid acid catalysts made from silica, such as sulfonated mesoporous silica-carbon catalysts, have been produced using TEOS or water glass.

In previous research, mesoporous silica-carbon catalysts were made using hydrocarbon compounds as carbon precursors or templates to create catalysts. In this study, PEG (polyethylene glycol) is used as both the carbon precursor and template to produce porous materials with a larger surface area, greater pore volume, and better thermal and chemical stability. Therefore, this research aims to produce a silica-carbon composite as a solid acid catalyst with good catalytic performance.

1.1 Heterogeneous solid acid catalysts

A catalyst is a substance that can increase the rate of a reaction without being consumed in the process. Catalysts are widely used in nature, industry, and laboratories, and it is estimated that they contribute to one-sixth of the value of all goods produced in a country's industry. Catalysts are classified as homogeneous if they are in the same phase as the reactants, which typically means that the catalyst is a solute in a liquid reaction mixture. On the other hand, catalysts are classified as heterogeneous if they are in a different phase from the reactants, which usually means the catalyst is in solid form while the reactants are in gas or liquid form. Catalysts play a role in engineering the kinetics of a reaction, with the goal of increasing or decreasing the reaction rate without affecting the reaction itself, as illustrated in (Fig. 1). Catalysts increase the reaction rate by lowering the Gibbs activation energy. In their role, catalysts work by reducing the energy barrier between reactants and products, allowing equilibrium to be reached more quickly than without a catalyst.

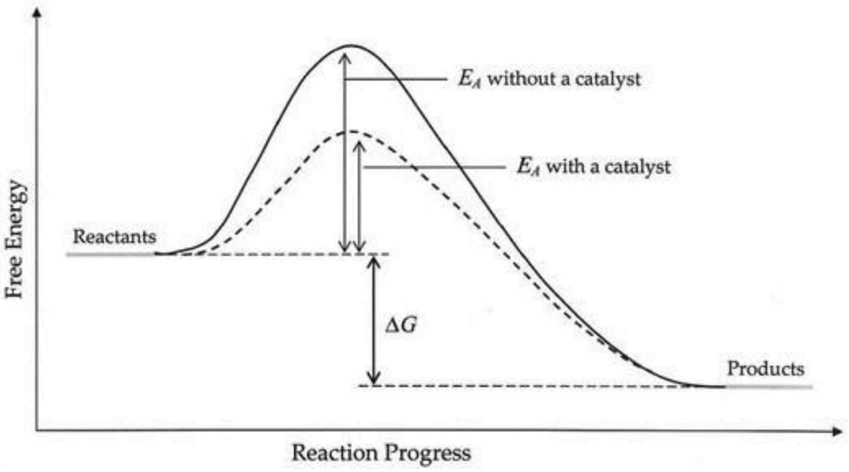


Fig. 1. The Relationship Between the Role of Catalysts in Chemical Reactions and Activation Energy

Solid acid catalysts are more effective than homogeneous acid catalysts, which require special handling to separate the catalyst from the product. Additionally, homogeneous catalysts also produce toxic residues, so these types of catalysts are increasingly being replaced by solid acid catalysts. Solid acid catalysts have the advantage of being easier to separate and can be reused in subsequent processes, helping to reduce environmental pollution (Ziarani et al., 2015). For these reasons, the development of solid acid catalysts has become an interesting focus, leading to catalysts that can be used in various applications, including in industries such as biodiesel production.

In catalyzing the esterification reaction in biodiesel production, solid acid catalysts must have certain characteristics, such as interconnected large pores, a relatively high concentration of strong acid sites, and a hydrophobic surface. The surface area of the catalyst influences its catalytic activity: the larger the surface area, the more active sites are available, which can increase catalytic activity and the resulting product yield. Surface area is one of the key factors in the effectiveness of heterogeneous catalysts, although it doesn't always directly correlate with catalytic activity. A larger surface area provides more contact between the reactant molecules and the catalyst, which influences the overall catalytic process. Reactant molecules will move freely before adsorbing onto the catalyst surface, where they become activated and react to form a product. Therefore, increasing the catalyst's surface area will lead to an increase in the number of active sites, and the opposite is also true.

1.2 Silica Gel

Silica is a compound formed by the polymerization of silicic acid, consisting of chains of SiO_4 tetrahedra with the general formula SiO_2. In nature, silica is found in several natural materials, such as sand, quartz, glass, and others. Naturally occurring silica has a crystalline structure, while synthetic silica is amorphous. Synthetic silica can be made from silicate solutions or silane reagents. Silica gel is one of the synthetic silica compounds with an amorphous structure. Silica gel is a solid chemical material widely used as an adsorbent. This is due to its ease of production and several other advantages, including: being highly inert, hydrophilic, having high thermal and mechanical stability, and relatively not swelling in organic solvents compared to organic polymer resin solids (Sulastri & Kristianingrum, 2010).

The pore structure in silica particles can be of two types: irregularly ordered and regularly ordered. The production of mesoporous silica particles with a regularly ordered structure can be done by adding a template. The template is used as a mold (a helper and guide) in the formation of pores, where the primary colloidal particles fill the gaps between the template structures. When the template is removed from the crystal, it results in hollow silica particles with an ordered structure. Based on the size of the main pores, IUPAC classifies porous materials into three categories: (1) microporous, with pore sizes < 2.0 nm, (2) mesoporous, with pore sizes 2 - 50 nm, and (3) macroporous, with pore sizes > 50 nm. To obtain regularly ordered pores or type 6 pores with an ordered arrangement, templates such as surfactants and polymers are typically used (Ziarani et al., 2015).

Silica gel is an amorphous silica composed of irregularly arranged SiO_4 tetrahedral globules that aggregate to form a larger three-dimensional framework. The general chemical formula of silica gel is $SiO_2.x\ H_2O$. The mineral silica unit structure essentially contains Si^{4+} cations coordinated tetrahedrally with O^{2-} anions. However, the tetrahedral SiO4 arrangement in silica gel is irregular, unlike the following structure. The properties of silica gel are determined by the orientation of the ends where the hydroxyl groups combine. Due to the irregular arrangement of the SiO_4 tetrahedral surface, the distribution of these groups per unit area is not a direct measure of silica gel's adsorption capacity, although silanol and siloxane groups are present on the silica gel surface. The adsorption capacity does not correlate with the number of silanol and siloxane groups on the surface of silica gel but depends on the distribution of OH groups per unit area of the adsorbent.

1.3 Sol-gel method

The sol-gel technique can be defined as the process of synthesizing inorganic polymer materials from molecular precursors that first dissolve in a liquid, then undergo hydrolysis to form a solid dispersed in the liquid (sol), followed by a condensation reaction to produce a solid network containing liquid (gel). This method is advantageous not only because it can be performed at room temperature but also due to its energy efficiency, the ability to minimize reduction or shrinkage from solvent evaporation, and its capacity to produce gel or powder materials with a high surface area. It can generate various types of inorganic products with high purity, including nanoporous materials, monodisperse particles, mixed metal oxide particles, and hybrid organic-inorganic materials. The material synthesized in powder form can be microcrystalline, nanocrystalline, or amorphous. Furthermore, using this method, other advantages include its broad applicability in various fields, such as for monoliths, coatings, films, fibers, aerogels, glass, ceramics, as well as hybrid materials, and it allows for control over particle size, crystallinity, and structural shape, so the gel can be molded into the desired final form.

The sol-gel process is a multi-purpose solution technique that was originally used for the production of inorganic materials such as ceramics and glass with high purity and homogeneity. Generally, this process involves the transition of the system from liquid (sol) to solid (gel) phase. The sol-gel process is typically divided into several stages: solution preparation, gel formation, aging, drying, and densification (Setyawan et al., 2015).

The process of silica gel formation from sodium silicate precursor using an acid catalyst involves several steps, including the hydrolysis of the precursor (sol formation) that occurs when a sodium metasilicate solution is hydrated, resulting in an acid silicate sol. The following reaction takes place.

$$Na_2SiO_3+3H_2O \leftrightarrow Si(OH)_4+NaOH \qquad \text{(Eq. 1)}$$

Next, a condensation or polymerization process (gel formation) occurs, where the formed monosilicic acid undergoes polymerization to form Si-O-Si cross-links. Silicic acid in water forms a dispersion of silicic acid known as hydrosol. Subsequently, the monomers of silicic acid will undergo condensation polymerization, forming dimers, trimers, and so on, eventually creating a polymer network of silicic acid. Since water is a by-product that can evaporate, the polycondensation stage results in the formation of a rigid three-dimensional network. This network is formed by the crosslinking of polymer molecules and is surrounded by solvent, referred to as a gel.

The sol-gel process offers the same benefits for producing high-purity porous silica with a density between 1.7 – 2.2 g/cc. The process performed under room conditions allows for the encapsulation of a range of organic, organometallic, biological molecules, and inorganic substances. In a specific sol-gel process, the precursor undergoes a series of hydrolysis and polymerization reactions to form a suspension. For the production of silica sol-gel, the gel network formation step is as follows:

$$Si–OH+OH–S \leftrightarrow Si–O–Si+H_2O \qquad \text{(Eq. 2)}$$

Gel formation depends on the pH or proton concentration in the solution. The condensation process occurs through a nucleophilic mechanism. Adding acid increases the proton (H+) concentration in the sodium silicate solution, causing some siloxy (Si–O–) groups to protonate and form silanol (Si–OH) groups. The acid typically used is hydrochloric acid, but using HCl results in the by-product NaCl, so excess water is needed during the washing process to remove the formed salt. To obtain the desired mechanical properties after gelation, the formed gel requires a gel aging process under specific conditions. During this stage, the polycondensation reaction continues to complete gel formation.

The gel prepared in the previous step will undergo aging in its parent solution. This aging process strengthens the gel, so shrinkage during the drying stage remains minimal. Increasing the aging time from 1 to 12 hours results in an increase in the surface area of the sample. The gel maturation process in alkogels involves a polymerization mechanism where the polycondensation reactions of monomers or oligomers in the gel network continue. Then, the syneresis mechanism occurs, where gel network shrinkage takes place due to excessive condensation reactions that involve the loss of liquid from the gel pores, and the coarsening mechanism, where the rigidity of the silica network and siloxane cross-links is enhanced without drastically modifying the pore size (Prasad & Pandey, 2012).

1.4 Freeze drying process

Freeze drying is a method of removing water by sublimating the crystalline ice from frozen materials. The appropriate process parameters for this application allow us to obtain products with the best quality compared to those dried using traditional methods.

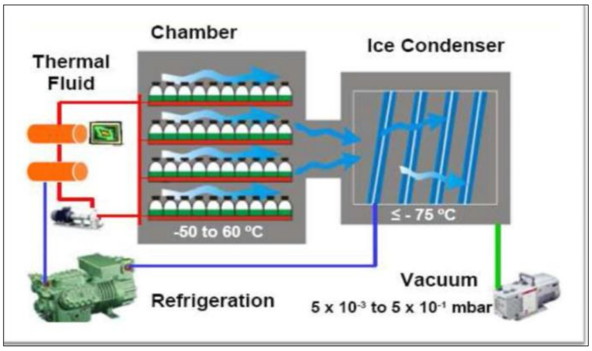


Fig. 2. Freeze Drying Equipment Setup

Freeze drying consists of three processes: freezing, primary drying, and secondary drying. Freeze drying is a well-established technology; however, it is costly. One of the primary objectives of freeze drying is to minimize drying time, but one of the stages, primary drying, is the longest of the three steps in the freeze drying process. This issue can be addressed by increasing the temperature during secondary drying. However, raising the temperature of secondary drying before all the ice has sublimated from the product may lead to collapse or brittleness of the product (Gaidhani et al., 2015).

The main principle involved in the freeze drying process is a phenomenon called sublimation, where water transitions directly from a solid state (ice) to a vapor state without passing through a liquid phase. Water sublimation can occur at pressures and temperatures below the triple point, for example, at 4.579 mm Hg and 0,0099 degrees Celsius. The material to be dried is first frozen (so products initially in liquid or gel form must first be frozen in a freezer) and then subjected to high vacuum and heat (through conduction, radiation, or both), so that the frozen liquid leaves behind only the solid and dry components. The vapor pressure gradient between the drying front and the condenser is the driving force for removing water during the freeze-drying process (Gaidhani et al., 2015).

1.5 Silica-carbon composite

A composite refers to the combination of two or more materials, one of which is a solid with different characteristics, resulting in performance parameters for various applications that are better and have more reliable material structural strength (Chawla, 1988). In this study, a silica-carbon composite was created to be used as a catalyst in the esterification reaction, which is one of the reactions in biodiesel production. The synthesis of mesoporous materials depends on certain conditions, such as the molar ratio of precursors, the type of material used as a template, the molar ratio of template/silica, aging time, temperature, and the composition of the source materials (Didik et al., 2010). Common materials used as templates in synthesizing mesoporous materials include surfactants, polymers, and biopolymers. The use of surfactants has been widely studied, but it is difficult to achieve good synthesis results due to the instability of the micelles when subjected to heat. This has led researchers to explore other materials with a high carbon source that can produce uniform silica-carbon mesoporous materials, which has gained significant interest (Kim et al., 2005). A uniform structure during gelation leads to uniform network growth during maturation, which can improve gel strength and its resistance to drying stress. Since the adsorption capacity of a substance is influenced by the surface area of the pores of a particle, a larger surface area results in higher adsorption capacity. In addition, the silica-carbon composite has stability against hydrothermal and mechanical changes.

One potential template for use in silica network formation is polyethylene glycol (PEG), which has surfactant-like properties that can form a framework, resulting in uniformity and regularity of the silica particle structure. Sun et al. (2002) and Sun et al. (2006) found that the largest surface area from various types of PEG was observed in PEG with a molecular weight of 2000, which allows the formation of both a porogen and framework in silica. However, PEG with a higher molecular weight tends to cause silica agglomeration, leading to complete encapsulation of silica by PEG, thus eliminating its role as a catalyst. Furthermore, Setyawan et al. (2015), reported the synthesis of mesoporous silica using polyethylene glycol 1000 as a carbon template, which was later removed using calcination and solvothermal methods. This resulted in a surface area of 340 m^2/g with the calcination method and 634m^2/g with the solvothermal method (Setyawan et al., 2015). Due to the significant surface area of this mesoporous silica, it has a considerable opportunity for functionalization in catalyst production.

After forming the PEG-silica hybrid, the porous silica can be obtained by removing the PEG template from the hybrid. Several methods are commonly used for template removal, such as calcination and supercritical fluid extraction. Calcination is a high-temperature burning or drying process, where the template is removed by oxidation. However, this process is energy-intensive due to the high temperatures required. Additionally, the process tends to cause sintering, a densification of the pore structure, and loss of mesostructure. With the significant characteristics of mesoporous silica, there is great potential for its functionalization in catalyst production.

1.6 Sulfonation process

Sulfonation is a process used to substitute a sulfonate group into the carbon chain of carbon-based materials formed by decomposition through high-temperature heating. Since an ideal catalyst for catalyzing the esterification reaction in biodiesel production requires a high concentration of strong acidic sites, modification is necessary. The introduction of sulfonate groups into a silica-carbon composite for sulfonation functionalization stabilizes the carbon framework, making it easier to separate the catalyst from the reaction system. This catalyst is synthesized through a sulfonation reaction, an electrophilic process, to modify chemical compounds by introducing sulfonate groups into the carbon chain, making the reaction quite complex due to the reversibility of the reaction.

The sulfonation process can damage the catalyst's pore structure, reducing its surface area because larger pores can allow the reactants to diffuse more easily into the catalyst's interior. However, this can lead to more intense contact between the reactants and the catalyst's acid sites, resulting in improved catalytic activity. Sulfonation of carbon material from pyrolysis produces a more stable solid with a high density of active sites. The sulfonated carbon, with stable carbon groups, is resistant to dissolution in either acidic or basic conditions, making it easy to separate the catalyst from the reaction and reuse it (Kang et al., 2013).

Sulfonation can be performed using chemicals containing sulfonate groups, such as sulfuric acid (H_2SO_4), chlorosulfonic acid (HSO_3Cl), and fuming sulfuric acid. The polymer chain is bound by the addition of sulfonate groups and the influence of SO_3 bonds during the sulfonation process. The size of the sulfonate group determines the torsion of the polymer chain around the carbon atom.

1.7 Adsorption and characterization of porous particles

The adsorption process can be described as a process in which molecules leave a solution and adhere to the surface of an adsorbent due to chemical and physical interactions. The adsorption mechanism consists of three stages. The first stage involves the diffusion of contaminant molecules to the adsorbent surface. The second stage involves the migration of contaminant molecules into the adsorbent's pores, and the third stage is the formation of a monolayer of adsorbate. The adsorption process depends on the properties of the solid that is adsorbing, the properties of the atoms/molecules being adsorbed, the concentration, temperature, and other factors. Adsorption equilibrium occurs when a solution is contacted with a solid adsorbent, and the adsorbate molecules move from the solution to the solid until the concentration of the adsorbate in the solution and the solid reaches equilibrium. The equilibrium phase between the liquid and the phase absorbed by one or more components in the adsorption process is a determining factor in the performance of the adsorption process. Equilibrium data at a certain temperature are usually shown by an adsorption isotherm, which represents the relationship between the amount adsorbed per unit mass of solid and the concentration of the adsorbate in the solution. To measure an adsorption isotherm, the amount of adsorbent and solution is contacted at a constant temperature, ensuring that the solution composition does not change over time. The adsorption isotherm can be calculated by measuring the adsorbate concentration in the solution at the beginning and at equilibrium.

Gas molecules that adhere to the solid surface (adsorbent) are absorbed and tend to form a thin layer covering the entire adsorbent surface. According to the Brunauer, Emmett, and Teller (BET) theory, the number of molecules needed to cover the adsorbent surface with a monolayer of adsorbed molecules (Nm) can be estimated. The surface area can be calculated by multiplying Nm by the cross-sectional area of the adsorbate molecule. The BET method calculates the specific surface area from adsorption isotherms using nitrogen as the adsorbate at 77 K. Almost all materials can be analyzed under these conditions, except for some micropores and materials with very low surface areas. While there are many alternative equations to describe the isotherm.

Pore volume is determined by the amount of gas adsorbed at relative pressure, assuming that the pores are filled with adsorbate. If the sample does not have macropores, the isotherm curve shows a horizontal line beyond the relative pressure. If the sample has macropores, the isotherm curve shows relative pressure = 1, and the maximum macropore limit shows a vertical increase. The volume of nitrogen adsorbed (Vads) can be converted into the liquid nitrogen volume (Vliq) contained in the pores.

Pore size distribution based on thermodynamics is measured using desorption isotherms. For nitrogen as the adsorbate at its normal boiling point of 77 K and using the previously provided physical properties, the procedure for calculating the pore distribution uses the Barret, Joyner, and Halenda (BJH) numerical integration method. This method incorporates Wheeler's theory that condensation occurs in pores when the relative pressure reaches the Kelvin radius (rk). This model also assumes that the thickness of the multilayer adsorbed film on the pore walls during condensation or evaporation is the same as the adsorbed film on non-porous surfaces.

Table 1. List of previous research

No	Researcher	Research
1	(Valle-vigón et al., 2012)	This research aims to produce sulfonated mesoporous silica-carbon composites as solid acid catalysts. The solid acid catalysts were synthesized from SBA-15 and KIT-6. The preparation of silica-carbon composites was carried out in two stages: the formation of silica gel followed by its composite formation with carbon.
2	(Wahyuni & Setyawan, 2013)	Synthesize sulfonated silica from waterglass using PEG as a template for solid acid catalysts. The study found that calcination was more effective in removing PEG templates compared to solvothermal extraction and examined the effect of PEG on the ion capacity of the catalyst.
3	(Hakim & Palupi, 2015)	Synthesize silica-carbon composites using waterglass as a silica source and sucrose with PEG as a carbon source. The research demonstrated that the concentrations of sucrose and PEG influence the surface area, pore diameter, and pore volume of the resulting silica-carbon composites.
4	(Barqi & Pertiwi, 2016)	The synthesis of silica-carbon solid acid catalysts (using PEG and sucrose impregnation) yielded the highest surface area and ion capacity values of 382.777 m^2/g and 2.15mmol/g, respectively.
5	(Fadli, 2019)	Preparation of silica-carbon composites using PEG as a template and carbon source. Surface area characterization was performed after sulfonation. The largest surface area was obtained at a temperature of 750°C for 1 hour, reaching 1651.477 m^2/g. From the ion capacity test, the highest ion capacity was achieved at 550°C, reaching 30 mEq/g.

2. Methods

2.1 General overview of the research

This research aims to study the synthesis of silica-carbon composites applied as acid catalysts. The silica-carbon composites were prepared through a sol-gel process. The process involved titration with 1 N NaOH until a pH of 4 was reached, forming a sol, which was then aged to form a gel. The gel was subsequently frozen in a freezer and dried through freeze-drying. The silica-PEG hybrid composite was then washed, dried in a desiccator, and calcined. Afterward, the silica-carbon composite was sulfonated to produce an acid catalyst based on silica-carbon composites, followed by washing and drying. Several factors influenced the process, including sulfonation temperature. After the formation of the solid acid catalyst, it was tested in esterification reactions. Key factors affecting the esterification process included the catalyst mass and esterification temperature.

2.2 Research materials

The synthesis of silica-carbon composites via the sol-gel method, using PEG as a templating agent and applied as acid catalysts, involved the use of several key materials. Waterglass with a composition of 28% (SiO_2:Na_2O = 3.3) was obtained from PT. Ineos Silicas Indonesia and served as the primary silica source. Hydrochloric acid (HCl) with a concentration of 37%, supplied by Mallinckrodt, was utilized as an acidifying agent in the sol-gel process. Demineralized water from PT. Brataco was used throughout the synthesis to ensure purity in the reactions. Additional acids included sulfuric acid (H_2SO_4) at 98% and glacial acetic acid at 100%, both procured from Merck. Absolute ethanol (99.5%), also from Merck, functioned as a solvent and played a role in gel formation. For gas chromatography (GC) analysis, standard solutions of glacial acetic acid, ethanol, and ethyl acetate were used, all of which were supplied by Sigma-Aldrich to ensure analytical accuracy and reliability in the characterization of the synthesized composites.

2.3.1 Synthesis of silica-carbon with PEG template

Fig. 3 shows the experimental diagram for synthesizing silica-carbon with PEG as a template.

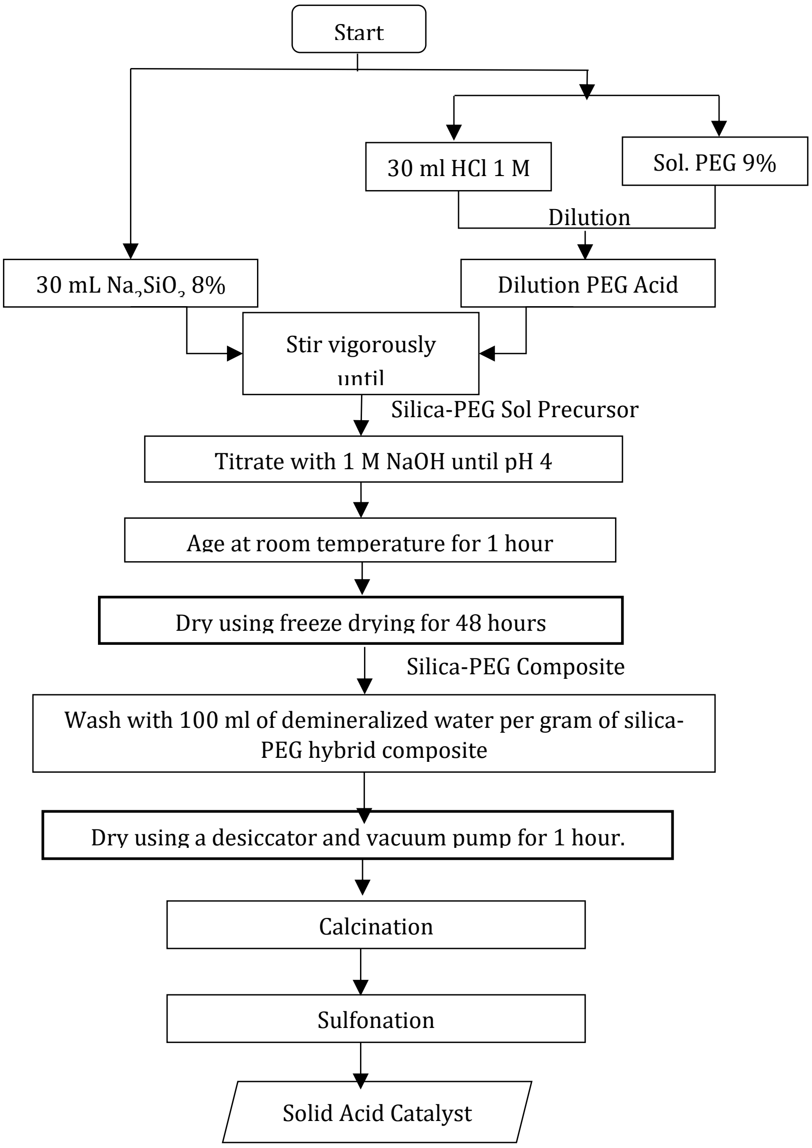


Fig. 3. Block Diagram of Silica-Carbon Synthesis Method with PEG

The first step is to prepare a waterglass (Na_2SiO_3) solution with a concentration of 8% SiO_2, made at 60°C to enhance the solubility of sodium silicate. The first step is to make a silica-PEG hybrid composite, which involves preparing a PEG 1000 acid solution by dissolving 3 g of PEG in 30 mL of demineralized water until the PEG dissolves homogeneously. Then, 45 mL of 1 M HCl solution is added to the PEG solution with vigorous stirring to produce the PEG acid solution. The next step is to mix 75 mL of the PEG acid solution, which functions as the template and carbon source in the silica-carbon composite, with 30 mL of the 8% SiO_2 waterglass solution, which functions as the precursor. The mixture is stirred vigorously to prevent gel formation. The silica-PEG sol solution is then titrated with a 1 M NaOH solution at a flow rate of 2 mL/min until the pH reaches 4, forming wet silica-PEG gel.

The resulting gel is aged in a desiccator for 1 hour, then placed in a freezer for 24 hours. After freezing, the gel is dried using freeze-drying for 48 hours to obtain dry gel. The dried gel is then washed with 100 mL of demineralized water per gram of the silica-PEG hybrid composite to remove NaCl salt formed as a residue in the silica-PEG hybrid composite. After that, the silica-PEG hybrid gel is dried again in a desiccator for 3 hours to produce dry silica-PEG hybrid composite.

2.3.2 Carbonization of silica gel

The silica-carbon composite is made by carbonizing the produced silica-PEG hybrid composite using a calcination method with nitrogen gas flow. The carbonization process is conducted in a tubular furnace using a pyrolysis reactor (Thermo Scientific Lindberg/Blue M Tube Furnace), which consists of a cylinder with a 1-inch diameter and a reactor length of approximately 30.5 cm, surrounded by refractory bricks. The equipment setup diagram can be seen in (Fig. 4). The inlet is connected to a nitrogen (N_2) gas tube with a rotameter to regulate the gas flow rate from the tube, while the outlet is connected to a vessel containing water to absorb the gas coming from the tube furnace, and there is a discharge valve to control the gas flow rate. The sample to be calcined is placed in a combustion boat, which is placed in the center of the tubular furnace.

Before the calcination process, purging is done by flowing N_2 gas at a rate of 150 mL/min for 15 minutes. This purging process aims to remove the existing O_2 gas. The calcination process for the composite with PEG is performed at 550ºC with a N_2 gas flow rate of 50 mL/min for 1 hour (the optimal calcination temperature and time based on previous studies) until the composite turns into a brownish-black silica-carbon composite. After the calcination process, the silica-carbon composite is cooled to room temperature, and characterization tests are performed, followed by the sulfonation process.

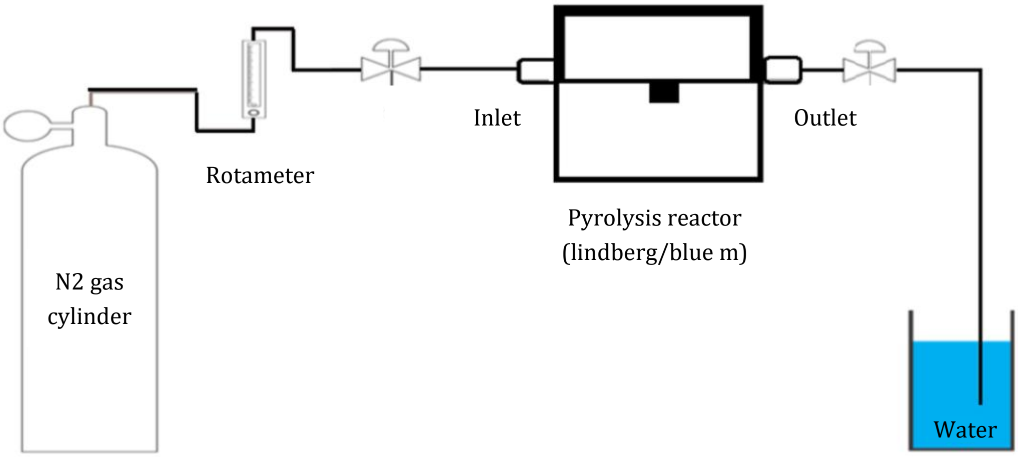


Fig. 4. Schematic Diagram of the Pyrolysis Reactor Setup (Linberg/Blue M Tube Furnace)

2.3.3 Sulfonation of silica-carbon composite

Sulfonation is carried out by placing the calcined silica-carbon composite into concentrated sulfuric acid (98%) solution, with a composition of 25 mL H_2SO_4 per gram of silica-carbon composite. Nitrogen gas (N_2) is then passed through for 45 minutes at a flow rate of 200 mL/min to remove O_2. The mixture is then heated at 100°C without N_2 flow to attach the -SO_3H group, forming an acid catalyst based on the silica-carbon composite. The mixture is then cooled to room temperature. The sulfonated silica-carbon composite is then washed with distilled water until the wash water is free of sulfuric acid solution and subsequently dried in a desiccator for 24 hours.

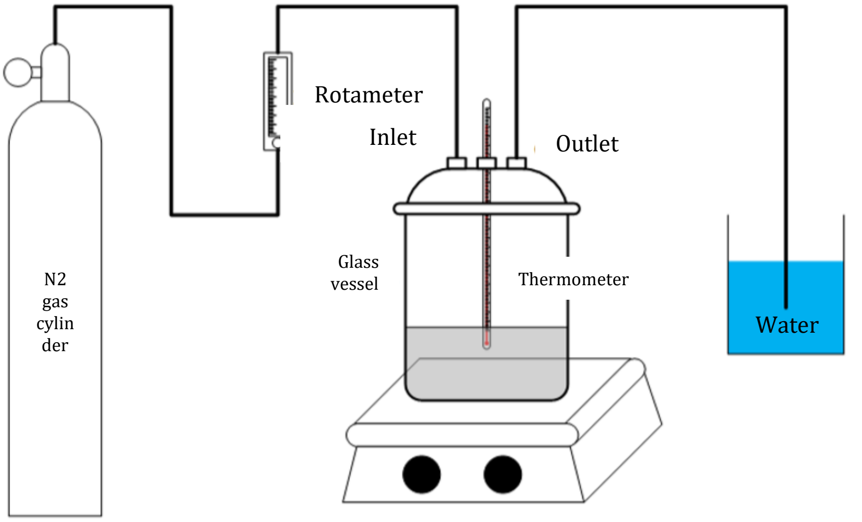


Fig. 5. Schematic Diagram of the Equipment Setup for the Sulfonation Process

2.4 Sample characterization

The characteristics of the silica-PEG hybrid composite, mesoporous silica-carbon composite, and sulfonated silica-carbon acid catalyst were analyzed for surface area and porosity using a surface area analyzer, surface morphology using scanning electron microscopy (SEM), functional group analysis using FT-IR spectroscopy, and catalyst performance, reusability, and activity using GC spectroscopy. The characterization of the products was carried out to observe the properties of the formed silica-carbon composite, including:

2.4.1 Characterization with nitrogen adsorption-desorption (surface area and pore size analyzer, quantachrome type NOVA 1200e)

The porosity of the silica material and silica-carbon composite, including specific surface area, pore volume, and pore diameter, can be analyzed through nitrogen adsorption-desorption isotherms at the boiling point of nitrogen (77K) using a BET (Surface Area and Pore Size Analyzer, Quantachrome type NOVA 1200e). Before measurement, the sample is degassed in flowing nitrogen at 300°C for 3 hours. The pore size distribution of the material is calculated during desorption using the Barret-Joyner-Halenda (BJH) method. The BJH method is the most commonly used method to calculate the pore size distribution in the mesopore range. The specific surface area is calculated using the multipoint Brunauer-Emmett-Teller (BET) method at $P/Po<0.3$, and the total pore volume is calculated using the P/Po approach.

Fig. 6. Nitrogen Adsorption-Desorption Test Equipment with BET Method (Quantachrome NOVA 1200e Surface Area and Pore Size Analyzer)

2.4.3 Morphological and composition characterization of products with SEM & EDX (SEM Phenom & PANalytical type minipal 4)

The morphology of the produced silica-carbon composite is tested using SEM (Scanning Electron Microscope) and the elemental composition of the composite is analyzed using EDX (Energy Dispersive X-Ray Analysis). This tool works by focusing high-energy electron beams to generate diffraction patterns on the sample's surface. The diffraction produces signals from the interaction of electrons with the sample, allowing the external morphology (texture), chemical composition, crystal structure, and orientation of the constituent materials to be observed. Before analysis, the sample is placed on an SEM pin attached with tape. The tape used can be either copper tape or carbon tape. Carbon tape is used for SEM analysis, while copper tape is used for EDX analysis. Coating is applied with PdAu (Palladium Gold) for EDX analysis and Carbon for SEM analysis.

2.4.4 Functional group characterization with fourier transform infrared (FTIR, Thermo Scientific Nicolet is10)

FTIR Spectrophotometry (Fourier Transform Infrared) is used to determine the functional groups contained in the produced silica gel composite. Essentially, the FTIR spectrophotometer is similar to a dispersive IR spectrophotometer, except for the development of its optical system before the infrared beam passes through the sample. This is based on the fact that atoms in a molecule do not remain stationary but vibrate. When infrared radiation with energy corresponding to the frequency of stretching and bending vibrations of covalent bonds in most molecules is passed through a sample, the molecules absorb this energy, causing transitions between the ground and excited vibrational energy levels. However, not all bonds in a molecule can absorb infrared energy, even if their radiation frequency matches the bond's movement. Only bonds with a dipole moment can absorb infrared radiation.

2.5 Catalyst performance test

2.5.1 Ion capacity and catalyst reaction test based on silica-carbon composite

The ion capacity of the sulfonated silica-carbon composite is determined by the acid-base titration method. A 0.2-gram sample of the sulfonated silica-carbon composite is soaked in 25 mL of 1 N NaOH solution for 48 hours. It is then titrated using 1 N HCl, and the volume of HCl required is calculated. The excess NaOH in the soaking process can be calculated from the HCl requirement during titration. The sulfonated silica-carbon composite produced is then used as an acid catalyst in the esterification reaction of acetic acid. This test is performed to determine the effectiveness of the silica-carbon composite as an acid catalyst. The test is conducted by reacting 40 mL of 99.5% ethanol and 20 mL of 100% glacial acetic acid in a three-necked flask equipped with a reflux condenser for 5 hours at temperatures of 80°C and 60°C. Samples are taken every half hour to determine the increase in ethyl acetate yield. The catalyst used in the reaction is 0.2 grams, 0.5 grams, and 0.8 grams.

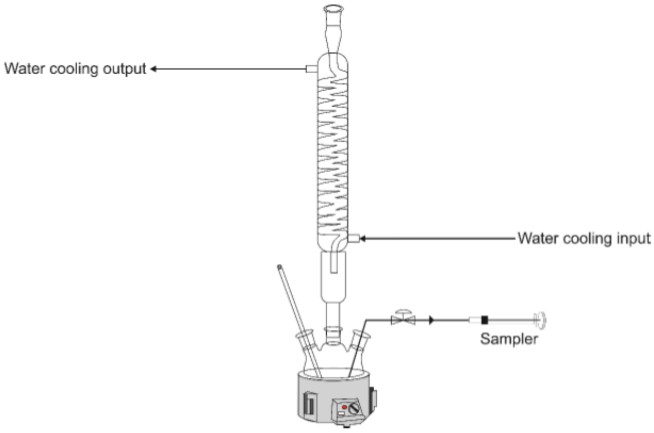


Fig. 7. Schematic Diagram of the Esterification Equipment Setup

2.5.2 Quantitative analysis using gas chromatography

The content of methyl stearate from the catalyst reaction test is analyzed using gas chromatography. Gas Chromatography (GC) is an instrument used for analyzing the content of various components in a sample. The mobile phase in GC is an inert gas (carrier gas) such as helium, argon, or nitrogen, and the stationary phase is a liquid. Almost all GC systems use a capillary column where the stationary phase coats the column walls. Component separation is based on the strength of the interaction between the components and the stationary phase. The stronger the interaction, the longer the time required to pass through the column (the retention time increases). The detector measures the quantity of components exiting the column. To measure a sample with an unknown concentration, a standard sample with a known concentration is injected into the GC instrument, and the retention time peaks of the standard sample are compared with the test sample to calculate the test sample's concentration.

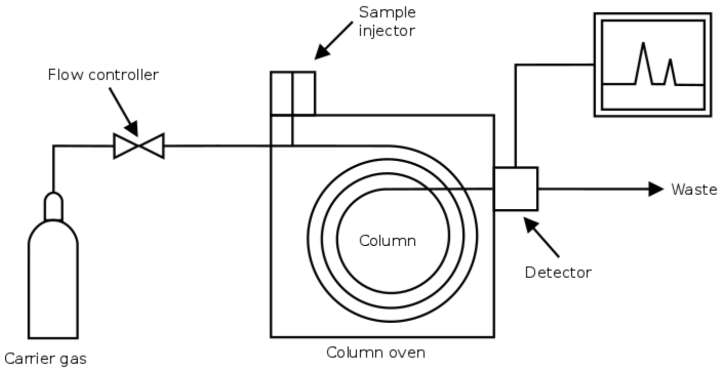


Fig. 8. Schematic Diagram of Gas Chromatography Test Setup

3. Results and Discussion

In this research, silica is an interesting focus because it has characteristics such as good thermal stability, inertness, and high mechanical strength. However, since silica only has active sites in the form of silanol and siloxane groups with low acidity, this study aims to modify the silica structure by combining silica with the organic polymer polyethylene glycol (PEG) to create a high-value material with more advantageous characteristics for application as a catalyst in esterification reactions. This study aims to investigate the effect of sulfonation temperature on the acid catalyst based on the silica-carbon composite produced, as well as the effect of the solid acid catalyst on the effectiveness of the esterification reaction. To study the incorporation of PEG into the silica network, we used the sol-gel method, which is the most effective method for producing silica composite materials with better material texture. The use of polymers such as polyethylene glycol (PEG) and inorganic materials (SiO2 from waterglass) in composites is known to provide good dispersion properties in solution and good thermal stability, making them suitable for various applications, especially in esterification reactions. The process was followed by carbonization through calcination to decompose the carbon source into carbon, forming a composite. After the silica-carbon composite was formed, sulfonation was carried out using concentrated sulfuric acid according to the determined temperature variables. Several characterization tests were then performed. To determine the material's porosity, including surface area, pore volume, and pore diameter, nitrogen adsorption/desorption was used. Morphology and elemental composition in the product were analyzed using SEM-EDX. Finally, FTIR characterization was performed to identify functional groups. To determine the characteristics of the produced catalyst, ion capacity and reaction tests were conducted. In this study, the performance of the produced catalyst was tested in the esterification reaction of acetic acid and ethanol with a volume ratio of 1:2 for 3 hours at temperatures ranging from 60 to 80°C, with sampling taken every 15 minutes to monitor the catalytic stability by tracking the conversion of acetic acid.

3.1 Characteristics of silica-carbon composite with PEG template

The preparation of the silica-carbon composite with a PEG template was done using the sol-gel method. During this process, a condensation reaction occurred in the sol-silica-PEG precursor solution, so that after titration and reaching a certain pH, the liquid in the solution changed to viscous and became gel-like. After aging, the gel that had solidified but still contained water was subjected to drying. In this research, drying was performed using the freeze-drying method instead of heat drying to prevent silica mass shrinkage during heating. (Fig. 9 (a)) below shows the physical appearance of the silica-PEG hybrid composite synthesized using the freeze-drying method.

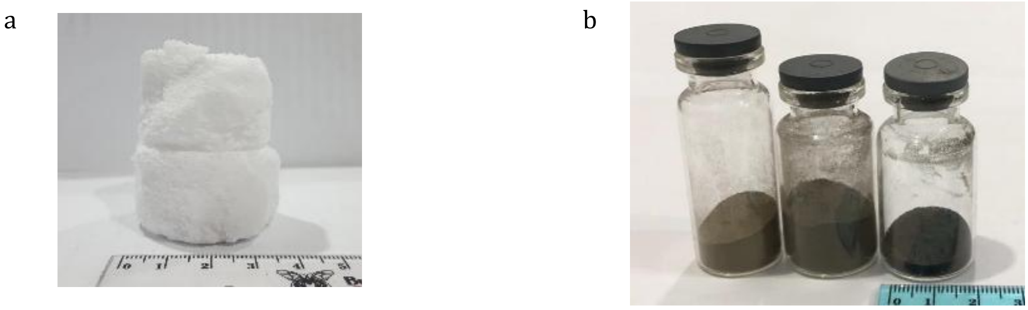


Fig. 9 (a) Silica-PEG Hybrid Composite After Freeze drying ; (b) Silica-Carbon Composite After Sulfonation Process

Based on (Fig. 9 (a)), it is seen that the freeze-dried Silica-PEG hybrid composite has a monolithic shape, white in color, with an intact structure that is able to maintain its shape. Meanwhile, (Fig. 9 (b))shows the result of sulfonation of the silica-carbon composite. The sulfonation process was carried out by immersing the calcined silica-carbon composite into concentrated sulfuric acid (98%) with a composition of 25 ml H_2SO_4/gram of silica-carbon composite. Then, nitrogen gas was passed through for 45 minutes at a rate of 200 ml/min to remove oxygen gas. Next, it was heated to 100°C without nitrogen flow to attach the -SO_3H group, thus forming an acid catalyst based on the silica-carbon composite.

3.2 Functional group characterization

The synthesized composite was analyzed using FTIR (Fourier Transform Infrared Spectroscopy) to identify the functional groups present in it. FTIR analysis was performed by passing infrared radiation through the sample so that the compounds within the sample could absorb this radiation at specific frequencies. The amount of energy absorbed by the compound affects the molecular state of the compound, as the infrared radiation energy is related to the energy required for bond vibrations. The energy required varies for each bond, and each bond absorbs at different frequencies in the infrared radiation. The FTIR analysis results in a spectrum that shows the percentage of transmittance at various infrared radiation frequencies, as shown in (Fig. 10).

Based on (Fig. 10), the absorbance spectrum of the silica sample shows the presence of a hydroxyl (O-H) group, which is evidenced by a broad peak at the wave number of 3400,50 cm-1. Additionally, an absorbance peak is observed at 956,69 cm-1, indicating the bending vibration of silanol (Si-OH). Various bond vibrations indicating the presence of siloxane (Si-O-Si) groups are also observed in the FTIR spectrum, marked by absorbance peaks at 457 cm-1, 796,60 cm-1, and 1082,07 cm-1. The sharp absorbance peak at 457 cm-1 indicates the rocking vibration mode of oxygen with silicon in the Si-O-Si bond group, the absorbance peak at 796,60 cm-1 shows the characteristic symmetric stretching vibration of the Si-O-Si bond, while the absorbance peak at 1082,07 cm-1 indicates the characteristic asymmetric stretching of the Si-O-Si bond. This data shows that there are numerous Si-O-Si bonds forming a network between each other, or in this case, it represents the silica gel formation process.

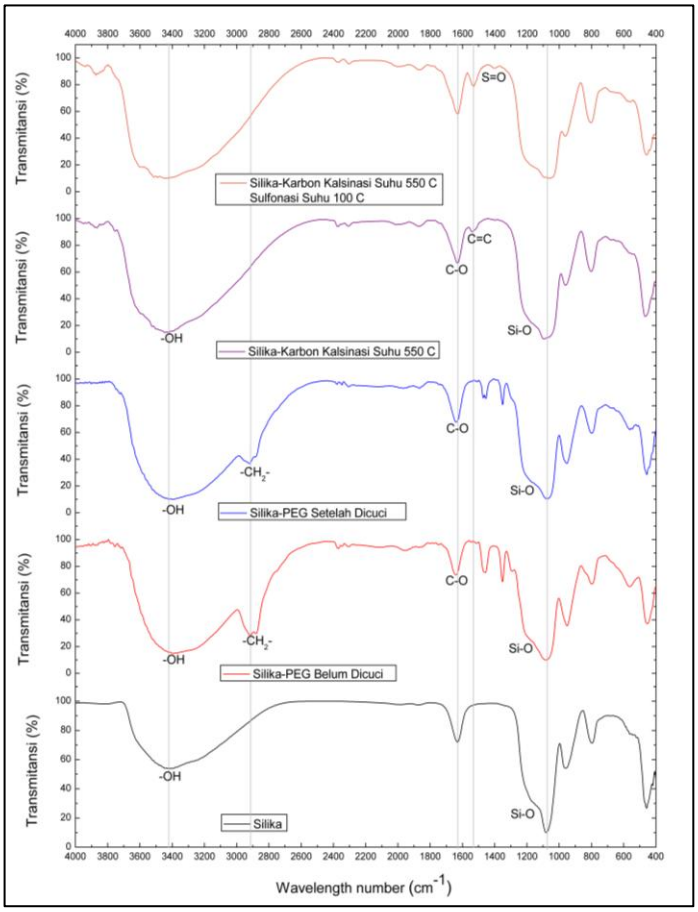


Fig. 10. FTIR Spectra of Silica, Silica-PEG, Silica-Carbon, and Sulfonated Silica-Carbon

The FTIR data for Silica-PEG samples, both washed and unwashed, show differences. A decrease in absorbance occurs after washing, specifically at the absorbance peaks at 1458.18 cm-1 and 1352.10 cm-1, which indicate C-H bonds from PEG. Upon careful examination, the FTIR spectra of Silica and Silica-PEG show that the absorption peaks of both silica and PEG are present in one spectrum, confirming the successful integration of PEG with silica to form a composite. The presence of PEG is indicated by the detection of carbon chain groups such as -CH2- at 2916,37 cm-1 and 2879,72 cm-1 and C-H bonds such as CH3 at 1458,18 cm-1 and 1352,10 cm-1. The presence of silica is indicated by silanol groups, proven by the absorbance peak at 3392,79 cm-1, 952,84 cm-1, and siloxane groups at 453,27 cm-1, 565,14 cm-1, and 798,53 cm-1.

The formed Silica-PEG hybrid composite then undergoes carbonization through calcination at 550°C, resulting in the formation of a Silica-Carbon composite. The transition to Silica-Carbon is confirmed by comparing the FTIR data of Silica-PEG and Silica-Carbon. Significant differences are observed, such as the disappearance of absorbance peaks at 1458,18 cm-1 and 1352,10 cm-1 (C-H bonds) and a decrease in peaks at 3392,79 cm-1 and 952,84 cm-1 (O-H bonds). The calcination process converts the composite to Silica-Carbon, supported by the appearance of a new absorbance peak at 1543,05 cm-1, indicating C=C bonds.

Sulfonation of the Silica-Carbon composite is performed at 100°C for 5 hours to generate the catalytic active site, represented by sulfonate groups. FTIR data confirm the successful grafting of the sulfonate group (-SO3H) into the composite, marked by the increase in the peak at 1403,5 cm-1, indicating the S=O bond. The FTIR characterization has successfully provided qualitative information about the presence of specific functional groups, confirming that the synthesized material is a Silica-Carbon composite with grafted sulfonate groups, which serve as active sites for catalysis.

3.3 Pore and surface area characterization (adsorption/desorption of silica-carbon composite with PEG template)

The Silica-Carbon composite with PEG template was characterized using nitrogen adsorption/desorption. The composite was analyzed using the Bruener-Emmet-Teller (BET) method.

Additionally, Table 2 shows that the influence of sulfonation temperature on the volume and pore size of the sulfonated silica-carbon catalyst can be observed. The pore volume produced at 100°C is the largest, with a total pore volume of 1.363 cc/gram, while at 80°C, a smaller pore volume of 0.9712 cc/gram is produced. At temperatures of 120°C, 135°C, and 150°C, the pore volume tends to decrease. This is because carbon particles shrink, causing the pore structure to collapse, and the voids formed are filled with carbon, resulting in a smaller surface area and pore volume. This supports the idea that as the surface area increases, there is also an increase in the total pore volume. It further confirms that the optimal sulfonation temperature based on surface area is 100°C.

Table 2. Pore characteristics of sulfonated acid catalyst at different sulfonation temperature variations

Temperature (°C)	Surface Area (m2/gram)	Total Pore Volume Characteristic (cc/gram)	Pore Diameter (nm)
80	803.836	0.9712	4.83271
100	1619.242	1.363	3.36791
120	608.604	0.17618	5.00663
135	770.388	0.8926	4.63477
150	468.934	0.1455	5.00663

Fig. 11 shows the effect of sulfonation temperature on the surface area of the resulting sulfonic acid catalyst. The curve indicates that as the sulfonation temperature increases, the surface area of the silica-carbon catalyst tends to decrease from a temperature of 100°C. However, when sulfonation is carried out at a lower temperature of 80°C, the resulting surface area is only 803.836 m^2/g, which is smaller than the surface area obtained at 100°C (1619.242 m^2/g), but larger than the surface area at higher temperatures above 100°C.

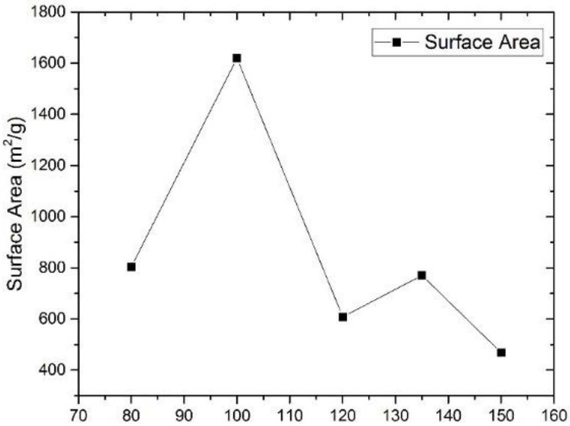


Fig. 11. Graph of the Effect of Sulfonation Temperature on Surface Area

3.4 Surface morphology and composition characterization

The effect of different sulfonation temperatures on the surface morphology of mesoporous silica-carbon composites was analyzed using SEM at a magnification of 10,000x. Morphology and composition analysis was also performed on the silica-PEG hybrid composite before and after washing, as well as on the mesoporous silica-carbon composite. The silica-carbon composite was also characterized using SEM-EDX to determine the elemental composition. Furthermore, the SEM-EDX test also serves to verify whether NaCl in the Silica-PEG Hybrid Composite has been removed after the washing process, by comparing the composition of the Silica-PEG Hybrid Composite before and after washing. Additionally, it was used to observe whether PEG as a template has decomposed completely after calcination at 550°C for 1 hour. Below are the composition analysis results for each compound.

Table 3. Element composition in the silica-PEG hybrid composite before and after the washing process

Element	%wt Before Washing	%wt After Washing
Si	20.74 %	33.98 %
O	24.74 %	39.03 %
C	47.13 %	25.75 %
Na	2.56 %	-
Cl	3.97 %	-
Cu	0.86 %	1.25 %

Based on the Table 4, it can be observed that the mass percentages of Si and O in the composite are quite similar. However, in terms of atomic percentage, the O content is twice as large as Si. This indicates that Si and O in the composite form SiO2 bonds. The composite also contains C (carbon), which is the result of PEG decomposition during calcination.

Table 4. Element composition in the mesoporous silica-carbon composite and silica-carbon sulfonic acid catalyst

Element	%wt Mesoporous Silica-Carbon Composite	%wt Silica-Carbon Sulfonic Acid Catalyst
Si	28.80 %	32.48 %
O	32.88 %	37.35 %
C	38.12 %	29.94 %
Na	-	-
Cl	-	-
Cu	-	-
S	-	0.24%

PEG decomposes into carbon, forming a thin carbon layer on the pores of the silica. This thin carbon layer was detected by X-ray when performing EDX testing. The first table confirms that the Na and Cl contents in the silica-PEG hybrid composite have been removed after the washing process. After the sulfonation process, which forms the sulfonated silica-carbon catalyst, all the Na, Cl, and Cu impurities have been eliminated, and the appearance of the S element confirms that the sulfonate group has been grafted into the silica-carbon composite.

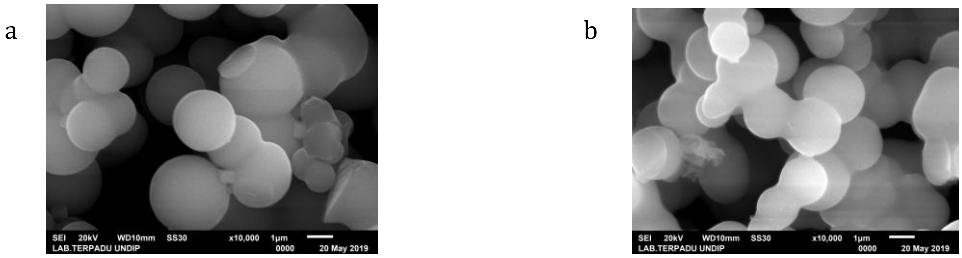


Fig. 12. SEM Image (a) Silica-PEG Hybrid Composite before washing ; (b) Silica-PEG Hybrid Composite after washing.

The particles of the Silica-PEG hybrid composite before washing have an average particle size of 3 μm, where almost all of the particles are irregular in size. Meanwhile, for the Silica-PEG composite particles after washing, the average particle size is 2.6 μm, and the overall particle size is much more uniform than before washing. After the washing process, the size of the Silica-PEG hybrid composite particles becomes smaller and more uniform because all the NaCl compounds have dissolved in the washing water. Initially, NaCl was combined with the siliceous acid compound in the hydrolysis reaction, making the resulting compound larger. The hydrolysis reaction mechanism for producing siliceous acid is as follows:

$$Na_2SiO_3 + H_2O + 2HCl \rightarrow Si(OH)_4 + 2NaCl \quad \text{(Eq. 3)}$$

After washing, the NaCl compounds have dissolved in the washing water, leaving behind only the pure Silica-PEG hybrid composite.

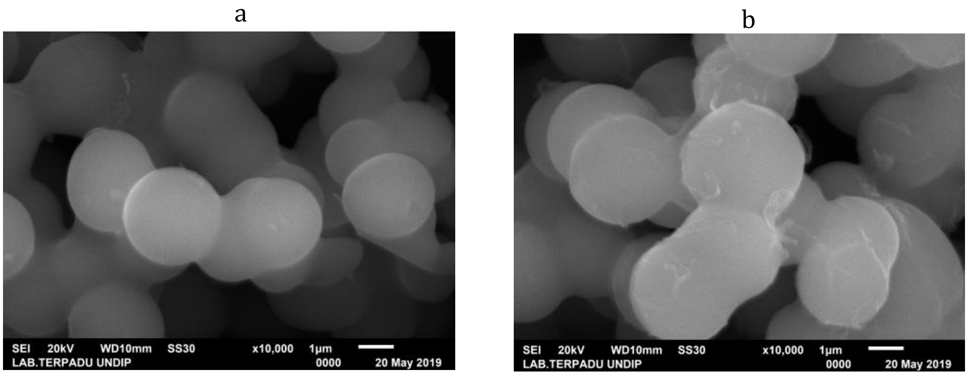


Fig. 13. SEM Image (a) Mesoporous Silica-Carbon Composite (b) Silica-Carbon Sulfonic Acid Catalyst

Sulfonation has more bonds and a more uniform structure compared to the silica-carbon sample before calcination, with an average particle size measured at 2.6 μm.

3.5 Sulfonate ion capacity test on silica-carbon sulfonic acid catalyst

To determine the amount of sulfonate ions grafted into the silica composite, refer to (Table 5.). The ion capacity of the sulfonated silica-carbon composite is determined using the acid-base titration method. A 0.2-gram sample of the sulfonated silica-carbon composite is soaked in 25 ml of 1 N NaOH solution for 48 hours. It is then titrated with 1 N HCl, and the volume of HCl required is calculated. The excess NaOH during the soaking process is calculated based on the amount of HCl needed in the titration process to determine how much excess NaOH was used in the soaking. The ion capacity (Ki) is determined from the amount of Na that reacts with $-SO_3H$ groups grafted onto the surface of silica, according to the following formula:

$$K_i\left(\frac{\text{mmol eq}}{\text{gr sample}}\right) = \frac{\text{mol NaOH that reacts with sulfonate}}{\text{gram sample}}$$

$$= \frac{(V_{\text{NaOH initial}} \times N_{\text{NaOH}})_{\text{initial}} - (V_{\text{HCl}} \times N_{\text{HCl}})_{\text{titration}}}{\text{gram of sulfonated silica-carbon composite}}$$

Based on Table 5, the catalyst treated with a sulfonation temperature of 100°C has the highest number of sulfonate ions compared to the sulfonation processes carried out at other temperature variables. This value is proportional to the larger surface area of a catalyst, which results in a higher sulfonate ion capacity. This is because the larger surface area of the catalyst increases the likelihood of having more active sites on the catalyst, thus increasing the chances of sulfonate groups being grafted onto the surface.

Table 5. Ion capacity value of silica-carbon sulfonic acid catalyst at various sulfonation temperature variables

Sulfonation Temperature Variable (°C)	Time (hours)	KI Value(meq/g)
150	48	10.5
135	48	6
120	48	4
100	48	12
80	48	9

Meanwhile, Fig. 14 shows that the KI graph tends to sharply decrease after 100°C, dropping steeply at 120°C, then gradually increasing again at 135°C. On the other hand, at temperatures below 100°C, the KI graph tends to decrease again starting at 80°C. This trend corresponds with the surface area at each temperature variable, where at temperatures above 100°C, the catalyst surface area tends to decrease, and as a result, the availability of active sites on the catalyst also decreases due to the shrinking of the sulfonate ion grafting sites. Based on the graph and table above, the optimum KI value is at a sulfonation temperature of 100°C, corresponding with the optimum surface area of the catalyst.

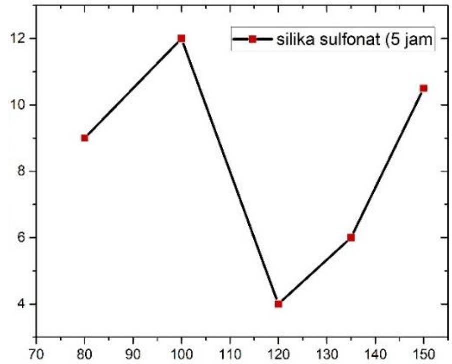


Fig. 14. Ion capacity of silica-carbon sulfonic acid catalyst at various sulfonation temperature variables

Ion capacity influences the catalyst's effectiveness. The higher the ion capacity, the more reactant molecules can enter the pores and react, making the catalyst more effective. High ion capacity indicates a higher ability to exchange H+ ions from strong acids, reflecting the number of sulfonate groups successfully grafted onto the silica-carbon composite surface. The sulfonate groups form chemical bonds on the composite surface, turning them into active sites for catalysis. The more active sites a catalyst has, the greater its ability to facilitate reactions, leading to higher conversion rates as the ion capacity increases.

3.6 Catalyst performance test based on silica-carbon composite

To determine the effectiveness of the silica-carbon composite as an acid catalyst, an analysis of the composite's performance in the esterification reaction was conducted. The esterification of acetic acid with ethanol was chosen to test the catalyst's performance. This test was carried out by reacting 40 mL of absolute ethanol (99.5%) and 20 mL of glacial acetic acid (100%) in a round-bottom flask equipped with a reflux condenser and magnetic stirrer for 3 hours at 80°C.

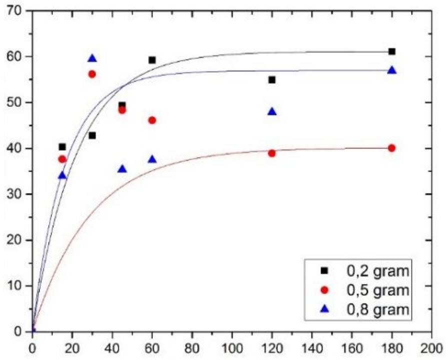
3.7 Effect of catalyst mass on the conversion of acetic acid

The effect of different catalyst masses on the conversion of acetic acid produced in the esterification reaction between acetic acid and ethanol, with a volume ratio of 1:2 at a temperature of 80°C, is shown in the following Table 6.

Table 6. Conversion results of acetic acid for various catalyst mass variables at esterification temperature of 80°C

Esterification Time (minute)	Acetic Acid Conversion (%)		
	0.2 gram	0.5 gram	0.8 gram
0	0	0	0
15	40.33	37.64	33.98
30	42.80	56.19	59.48
45	49.34	48.34	35.40
60	59.19	46.13	37.46
120	54.96	38.88	47.91
180	61.12	40.07	56.95

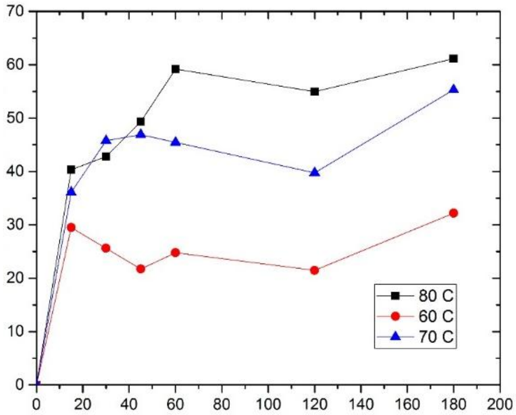
Based on Table 6, it can be seen that the highest and most stable acetic acid conversion results occur when the catalyst mass is 0.2 grams. Therefore, for subsequent esterification reactions, the catalyst mass of 0.2 grams is used to determine the effect of temperature on catalyst performance. Based on the graph in (Fig. 15), it is shown that a catalyst load of 0.2 grams yields the best results, and the conversion does not increase compared to the use of 0.5 and 0.8 grams of catalyst. This is likely due to the fact that when the catalyst mass exceeds 0.2 grams (0.5 and 0.8 grams), improper mixing occurs because the catalyst's solid density in the solution becomes quite high, reducing the contact area between the catalyst and the reactants. This is supported by Jagadeeswariah (2010), who states that a small, sufficient amount of catalyst can achieve maximum conversion (Jagadeeswaraiah et al., 2010).



(Fig. 15) The performance of different catalyst masses on the conversion of acetic acid produced (acetic acid:ethanol volume ratio=1:2, esterification temperature: 80°C)

3.8 Effect of temperature on acetic acid conversion

The conversion of acetic acid with respect to the esterification reaction time using the silica-carbon sulfonic acid catalyst at different reaction temperatures is shown in (Fig. 16). The mass of the silica-carbon sulfonic acid catalyst used is based on the highest acetic acid conversion obtained from other catalyst mass variables, which is 0.2 grams. The esterification reaction temperatures varied from 60°C to 80°C. As shown in (Fig. 16), as the esterification reaction temperature increases, the conversion of acetic acid also increases.



(Fig. 16) Performance of Silica-Carbon Sulfonic Acid Catalyst on the Conversion of Acetic Acid Produced at Different Esterification Reaction Temperatures.

Based on (Fig. 16), it shows that the conversion of acetic acid increases with increasing temperature. This is due to the effect of temperature on the internal energy of the molecules. At higher temperatures, the molecules in the reactor move faster, and the intensity of collisions increases. As a result, the reaction can proceed faster, leading to a higher yield, meaning the conversion of acetic acid to ethyl acetate becomes higher. However, this temperature increase will not always lead to a higher acetic acid conversion, as further temperature increases may cause the conversion to decrease. This decrease occurs because at 70°C, the temperature exceeds the boiling point of ethanol (78°C), causing some of the ethanol to undergo a phase change from liquid to gas. The phase change of ethanol reduces the amount of ethanol in the liquid phase, which in turn decreases the number of effective collisions required to produce ethyl acetate, causing the conversion of acetic acid to decrease (Prihanto & Irawan, 2018).

Furthermore, as the esterification reaction time increases, the acetic acid conversion at all three temperature variables continues to increase with longer esterification times, as shown in (Fig. 16). This is because reaction time significantly influences the conversion obtained: the longer the reaction time, the higher the conversion, as the chances of collisions between reactant molecules become greater. In Figure IV.8, with a reaction time of 60 minutes, the conversion of acetic acid reaches its most optimal result, but tends to stabilize or even decrease after 60 minutes of esterification. This happens because after 60 minutes, equilibrium has been reached, and extending the reaction time no longer provides significant benefits or improvements in conversion (Parhusip et al., 2012).

4. Conclusions

Based on the research findings, it can be concluded that the sulfonation temperature significantly influences the characteristics of the resulting silica-carbon composite. Notably, the optimal conditions for achieving the largest surface area and pore volume were found in the silica-carbon-based acid catalyst subjected to a calcination temperature of 550°C for 1 hour and a sulfonation temperature of 100°C for 5 hours. Under these conditions, the catalyst exhibited a surface area of 1619.242 m^2/gram, a pore volume of 1.363 cc/gram, and a pore diameter of 3.36791 nm. Furthermore, the highest ion exchange capacity, measuring

12 meq/gram, was also obtained at the same sulfonation temperature and duration, highlighting the effectiveness of these parameters in enhancing the catalyst's functional properties.

In addition, the study determined that the most effective catalyst loading for the esterification reaction between ethanol and acetic acid, with a volume ratio of 2:1, was 0.2 grams at a reaction temperature of 80°C. Under these conditions, the reaction reached an equilibrium conversion of 59.19%, indicating that this catalyst dosage and temperature provide the most efficient performance for the esterification process.

Based on the research conducted, several suggestions are proposed for the future development of silica-carbon-based acid catalysts. First, it is recommended to perform catalyst performance tests focused on reusability by applying the catalyst in repeated cycles of the same esterification reaction. This would allow for the evaluation of the catalyst's stability and effectiveness over multiple uses. Additionally, to further explore its practical applications, it is suggested to implement the use of solid acid catalysts on an industrial scale, particularly in biodiesel production processes. Scaling up to factory-level operations could provide valuable insights into the catalyst's performance under real-world conditions and its potential for commercial viability.

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Author Contribution

All authors have equally contributed to the conception, writing, and revision of this article, ensuring its accuracy and integrity.

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Conflicts of Interest

The authors declare no conflict of interest.

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