



Synthesis of Isoprene from Cracking of Natural Rubber at Low Temperature using Catalyst K_2O/KNO_3 and Solvent Diethyl Phthalate

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Abstract

Synthesis of isoprene so far formed from polymer conversion occurs at temperatures above 400°C with a percentage of less than 20% isoprene composition and is prone to forming other compounds such as aromatic compounds. This study aims to see if the use of K_2O/KNO_3 in converting natural rubber into isoprene will increase conversion and take place at low temperatures. KNO_3 can keep the formation of other side products with a composition of %, which aims to stabilize the catalyst to isolate the formation of isoprene. The results showed that variations in the amount of catalyst, temperature, and solvent in the cracking reaction significantly impacted the final result of isoprene synthesis. At 90°C, with the amount of catalyst 3 g, a conversion of 86.86% was obtained. This was due to the role of KNO_3 in stabilizing and increasing the catalytic activity of the catalyst. At 130°C, it produced a conversion of 1.5 g 81.58%. K_2O/KNO_3 catalyst can be amphoteric, basic, or acidic, influenced by the operating temperature. K_2O/KNO_3 catalyst in alkaline conditions has high stability and catalytic activity and can produce better conversion with low temperatures in natural rubber cracking to produce isoprene.

Keywords: Natural rubber, Cracking process, Isoprene, Potassium oxide, Potassium Nitrate, Diethyl Phthalate.

1. Introduction

Utilization of natural rubber resources for more economic value can be developed by converting it into new high-value products. Conversion of natural rubber involves thermal changes (heat) that cause natural rubber to undergo chemical transformation into different products [1]. This thermochemical process can include several chemical reactions, such as Pyrolysis, gasification, and oxidation, which can convert natural rubber into fuels, gases, liquids, or other chemical compounds [2].

In pyrolysis, natural rubber will undergo a cracking process to form isoprene, which requires the help of catalysts and solvents [3]. Research in recent

years has revealed various pyrolysis cracking processes. Pyrolysis research of waste tires uses a fixed bed reactor with metal catalysts Ni/SiO_2 , Co/SiO_2 , and Pd/SiO_2 at 350°C. Pd/SiO_2 catalyst is the most selective to aromatic compounds (about 40%) [4]. NR, BR, and SBR pyrolysis processes where pyrolysis temperatures below 390°C will form olefins, while higher temperatures will form aromatics [5]. Pyrolysis of waste rubber occurs at 400-700°C. Pyrolysis of waste automobile tires shows isoprene as the main compound formed at temperatures below 500°C [6].

The natural rubber cracking process will involve catalysts to streamline the reaction [7]. K_2O catalyst has potential in natural rubber cracking due to its positive effects in various reactions. Research on

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$K_2O/MgO-SBA-15$ catalyst showed good thermal stability and catalytic activity at $550^\circ C$ for 3 hours [8]. Research on waste cooking palm oil (WCPO) shows it is used as raw material to produce biofuel using a K_2O-MgO/CaO base catalyst. K_2O increases the yield of liquid pyrolytic products and significantly reduces oxygen compounds in biofuel through deoxygenation to improve biofuel quality. In contrast to the high reaction temperature, pyrolysis oil yields around 92% by volume at a reaction temperature of $500^\circ C$ [9].

In addition to K_2O , KNO_3 also shows excellent catalytic performance as a catalyst, such as in the cracking of rubber seed oil, resulting in a conversion of about 93.2% and a liquid hydrocarbon biofuel yield of 78.3% with a KNO_3 catalyst [9]. KNO_3 improved selectivity in the methylation process of cyclopentadiene on a mixture of $KNO_3/\gamma-Al_2O_3$ catalysts with 86% conversion [10]. Catalytic cracking of polystyrene waste with fly ash/ KNO_3 catalyst increased the maximum liquid yield to 88.4%. [11].

Combining K_2O catalyst with KNO_3 in K_2O/KNO_3 with a percentage ratio of % can crack natural rubber into isoprene well. Therefore, this research will use a K_2O/KNO_3 catalyst to crack natural rubber with a review that can occur below $150^\circ C$. The presence of KNO_3 in the K_2O/KNO_3 catalyst can stabilize and isolate the desired isoprene product so that no side products are formed.

2. Material and Method

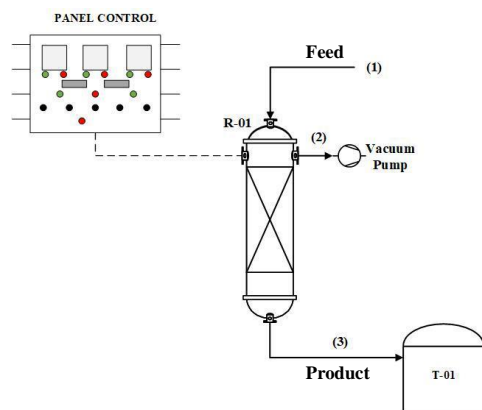
2.1. Material

SIR-10 natural rubber material is from PT Sri Trang Lingga Indonesia, K_2O/KNO_3 catalyst from Meroke Kalinitra, and Diethyl Phthalate (DEP) solvent is from PT Anugrah Visi Cemerlang.

2.2. Application of catalyst K_2O/KNO_3 and solvent Diethyl Phthalate (DEP)

Potassium oxide catalyst was mixed into Diethyl Phthalate (DEP) solvent solution with varied catalysts (0.5g, 1g, 1.5g, 2g, 2.5g, and 3g). Natural rubber raw materials were size reduced to 1g in weight. Raw materials and catalysts that have been prepared are put into a fixed bed reactor, and then vacuum conditions are carried out with a vacuum pump for 10 minutes until the pressure is constant at 0.8 inHg. The reactor was set with varied

temperatures ($90^\circ C$, $110^\circ C$, and $130^\circ C$) and a reaction time of 60 minutes. The constant temperature reactor was cooled to room temperature after the reaction time. Liquid samples were taken and analyzed for product composition using GC-FID analysis.



Scheme 1. Natural rubber pyrolysis process with K_2O catalyst

2.3. Analysis Stage

Product composition analysis was conducted using a Shimadzu GC-2014-AOC-20i FID Gas Chromatography.

3. Result and Discussion

3.1. Effect of Catalyst Amount on the Cracking Reaction of Natural Rubber SIR 10 to Isoprene

Variation of the amount of catalyst is very influential on the yield composition of isoprene, where adding the amount of catalyst to the yield composition will increase the percentage of % isoprene composition. At a temperature of $90^\circ C$, the increase in the number of catalysts is very influential on the composition of isoprene at the number of catalysts 2 g by 64.93% and most increased at the number of catalysts 3 g by 86.86%. However, the amount of 1.5 g and 2.5 decreased isoprene composition due to the chemical structure of the catalyst does not work well due to the amount of catalyst that does not have a good structure. At a temperature of $110^\circ C$, the effect of the amount of catalyst with the composition, including a minor composition of isoprene, can be caused. There are still many other product contents formed, and the transition of operating conditions from a temperature of $90^\circ C$ to $130^\circ C$.

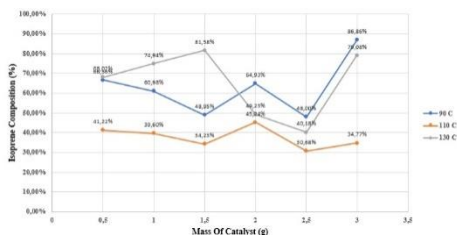


Fig 1. Graph of Catalyst Mass Addition against % Isoprene Composition

This shows that the use of catalysts in cracking reactions can also provide adjustments to product selectivity, such as increasing the selectivity of isoprene compounds and helping to increase the ratio to the amount of catalyst and composition [12]. K_2O , as a promoter, improves the catalyst's activity and selectivity [8]. In this case, K_2O/KNO_3 can direct the reaction towards forming isoprene by inhibiting side reactions that produce other products under suitable temperatures and catalyst conditions.

The highest isoprene composition at a temperature of 130°C occurred at the amount of catalyst 1.5 g with a percent composition of 81.56%, with the lowest percent at catalyst 2.5 g at 48.00%. At a temperature of 90°C, the increase in the amount of catalyst dramatically affects the composition of isoprene at the amount of catalyst 2 g by 64.93% and most increased at the amount of catalyst 3 g by 86.86%. At a temperature of 110°C, the effect of the amount of catalyst with the composition, including the minor conversion of isoprene, can be caused. There are still many other products formed, and operating conditions are transitioned from a temperature of 90°C to 130°C.

Increasing the amount of catalyst will significantly affect the temperature conditions of 90°C in forming isoprene composition results. However, at a temperature of 130°C, the increasing amount of catalyst will form other products, and the resulting isoprene composition decreases. Based on the data generated in the cracking of natural rubber using K_2O/KNO_3 catalysts, 86.86% results were obtained with a raw material and catalyst ratio of 1:3 at a temperature of 90°C and 81.56% with a raw material and catalyst ratio of 1:1.5 at a temperature of 130°C [13].

3.2. Effect of Temperature on the Cracking Reaction of Natural Rubber SIR 10 to Isoprene

In Figure 2, it can be seen that there is a fluctuating movement on increasing the reaction temperature. When the amount of catalyst 2.5 g is

added, the % composition when the reaction temperature occurs at 90°C, 110°C, and 130°C is less stable and increases and decreases than the other catalyst amounts of 48.00%, 30.68%, and 40.18%. The increase occurs due to the base catalyst that will release electrons and absorb protons in a higher reaction so that the base catalyst tends to take place in low operating conditions so that the pH of the catalyst is maintained in alkaline conditions. This is shown at a temperature of 90°C. The composition of isoprene produced reached 86.86% with the amount of catalyst 3 g. However, with the process occurring at low temperatures, the formation of isoprene requires a more significant amount of catalyst, so the yield composition will be directly proportional to the effect of temperature and the amount of catalyst.

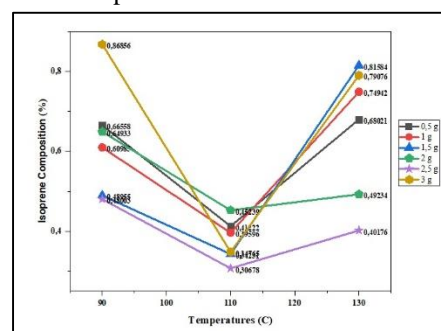


Fig 2. Temperature Increase with % Isoprene Composition

The highest increase and decrease in composition occurred when adding 3 g of K_2O/KNO_3 catalyst when the reaction temperatures were 90°C, 110°C, and 130°C. The composition of isoprene was 86.86%, 34.77%, 79.08%. Reaction temperatures that can occur by natural rubber cracking reactions that produce many products are influenced by temperature. In some studies, the results of cracking natural rubber into pyrolysis oil products, one of which is isoprene, are produced at temperatures above 400°C.

The role of the catalyst in the reaction is to make the reaction capable of taking place under low operating temperature conditions. The acidity of a catalyst plays a role in the reaction temperature. Generally, the K_2O/KNO_3 catalyst will be acidic with an increased temperature so that the catalyst will release protons and absorb electrons. The higher the reaction temperature, the easier the K_2O/KNO_3 catalyst will be to release protons and its high electron absorption rate. However, at low temperatures, the K_2O/KNO_3 catalyst will remain in a primary condition that serves to release electrons in helping the cracking process of natural rubber into

isoprene. So, the base catalyst tends to occur in low operating conditions where the proton absorption and electron release levels will be higher. Catalytic cracking on base catalysts occurs through a free radical mechanism. The formation of free radicals on the catalyst surface can occur at lower temperatures [12].

Therefore, isoprene conversion is large with a base catalyst, occurs at a low temperature, and a more significant amount of catalyst and few by-products are formed. K_2O/KNO_3 catalyst conversion will turn acidic and produce high by-products, but the amount of K_2O/KNO_3 catalyst requirement is reduced.

At a temperature of 110°C, a decrease in conversion is due to the higher temperature, which can cause the formation of aromatic compounds and increase the risk of side reactions. This shows that the K_2O/KNO_3 catalyst transitions from a primary to an acid catalyst. K_2O can become an acid catalyst at high temperatures and remain a primary catalyst at low temperatures. This is because the primary surface of K_2O can suppress the surface activity of acid sites and occurs in specific reactions. Thus, it can be seen from Figure 2. The temperature of 130°C has increased conversion due to the base catalyst forming an acid, so the capture of radicals by isoprene or natural rubber can release electrons. Thus increasing the yield of isoprene products at high temperatures with fewer catalysts.

Pyrolysis of waste tires under vacuum conditions (25 and 50 kPa) with a temperature of 500°C produced an isoprene composition of 7% [14]. This shows that the operating temperature in this study is somewhat lower than previous studies, such as in research [15] that used a single K_2O catalyst to convert polymers into monomers using a temperature of 350°C and rubber seed oil cracking research using $K_2O/MgO-SBA-15$ catalyst took place at a temperature of 550°C.

Acidity can also affect the increase in conversion at a temperature of 130°C. Acidity will increase due to an increase in temperature, so the ability of metal oxides to become acids and bases can increase acidity in metals. So, at a temperature of 130°C, there is an increase in the % composition of isoprene, but the catalyst K_2O/KNO_3 is no longer in alkaline conditions but already in acidic conditions.

At higher temperatures, the percentage yield of liquid products will decrease, indicating that the components that make up natural rubber are most

decomposed at that temperature. This is because, during the pyrolysis and cracking process, the bonds of long-chain hydrocarbon compounds contained in natural rubber will be broken so that they will lose their mass [16]. Higher temperatures can increase the risk of side reactions that produce unwanted or harmful products, such as polymerization.

The effect of operational parameters on the catalytic cracking of natural rubber shows that high temperatures can increase the formation of other aromatic compounds. This is because the higher the temperature in the reactor, the faster the secondary reactions, such as cyclization, dehydrogenation, aromatization, and the formation of aliphatic components. High cracking temperatures will increase cyclic and aromatic products, while low cracking temperatures will increase non-cyclic products [17].

3.3. Effect of KNO_3 on K_2O Catalyst for Cracking Reaction of Natural Rubber SIR 10 to Isoprene

The influence of KNO_3 is vital to the yield of isoprene composition. Providing an appropriate amount of KNO_3 to K_2O/KNO_3 can improve the catalytic activity of K_2O in the reaction to convert natural rubber into isoprene products—the ability of the K_2O catalyst to increase stability and catalytic activity by adding KNO_3 [18]. On the K_2O/KNO_3 catalyst, KNO_3 can boost the catalyst's efficiency, function as a catalytic promoter, or increase the availability of active sites on the catalyst surface. It can maintain catalyst stability and isolate the desired isoprene product in cracking. The appropriate composition of KNO_3 can also maintain the catalyst's pH to remain alkaline to transfer electrons to help the natural rubber-cracking reaction process. If the amount of KNO_3 is too excessive, it can cause the results of the isoprene composition to decrease. Adding KNO_3 in excessive amounts can affect the catalytic activity of K_2O . This occurs because excessive additions can affect the isoprene composition. This happens because excessive addition can inhibit the nature of catalyst activity.

It can be seen from the temperature of 90°C, with the amount of catalyst 0.5 g to 1.5 g experiencing a decrease in composition from 66.56%, 60.98%, and 48.95%, which can be caused by the effect of the addition of KNO_3 , which is more than the catalyst K_2O so that the resulting composition can decrease. This decrease can also be caused by the excessive addition of KNO_3 , which is detrimental to the reaction because it can lead to the formation of other decomposed aromatic compounds [18]. Adding

KNO₃ to the appropriate K₂O catalyst will result in good selectivity and increased conversion, occurring at a temperature of 90°C with a catalyst of 3 g, which increased by 86.86%.

The decrease in % composition is because the activeness of the catalyst used directly influences the number of products produced from catalytic cracking. Thus, it will reduce the composition of isoprene formation and produce other compounds. If excessive KNO₃ can cause the catalytic activity to decrease, KNO₃ also affects the temperature that increases as a catalyst promoter can affect the dehydrogenation of aromatic compounds [19].

At a temperature of 110°C, the conversion decreased significantly. This is because KNO₃ and K₂O cannot help the reaction optimally. After all, they are in an unstable pH state between acids or bases, so the yield of isoprene products has decreased significantly, producing a small conversion.

At a temperature of 130°C, there was an increase in the yield of isoprene composition at 0.5 g to 1.5 g of 68.02%, 74.94%, and 81.58%. This increase occurred due to the role of KNO₃ in maintaining good acidity conditions on the catalyst so that K₂O will maintain acidity to increase catalytic activity and produce a high-yield composition. The amount of catalyst 2 and 2.5 g decreased due to the factor of excessive KNO₃ so that it can cause damage to the pores of the catalyst surface, which results in the K₂O catalyst that reacts on the catalyst surface will be reduced [20].

4. Conclusion

K₂O/KNO₃ catalyst can be used at low operating temperatures where the highest percent composition on cracking natural rubber into Isoprene occurs at a temperature of 90°C with the amount of catalyst K₂O/KNO₃ as much as 3 g with a percentage of 86.86%. The lowest percent composition of natural rubber cracking into Isoprene occurred at a temperature of 110°C with the amount of catalyst K₂O/KNO₃ as much as 2.5 g at 30.68%. KNO₃ on the K₂O/KNO₃ catalyst plays a vital role in maintaining pH conditions as well as catalytic activity and high selectivity on the catalyst to help the process of cracking natural rubber into isoprene.

5. Conflict of Interest

The authors declare that the article content has no conflict of interest.

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