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THE CONVERSION OF BIOETHANOL FROM PINEAPPLE WASTE TO BIOBUTANOL DERIVATIVES OVER $NiMoO_4$/rGo CATALYST

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ABSTRACT

Increasing demand for sustainable energy solutions has spurred the development of catalytic materials to convert renewable resources into value-added hydrocarbons. In this work, we investigate the feasibility of $NiMoO_4$/rGo as an effective catalyst for converting bioethanol into renewable hydrocarbons. The surface and microstructural characteristics of rGo showed major findings like BET surface area of 26.9 m^2/g with mesoporous, sufficient surface functional groups, crystalline size of 49.12 nm, and a progressive metal oxide uniform distribution on the $NiMoO_4$/rGo surface. The crystal morphology showed an irregular texture, suggesting strong catalytic activity. The optimal conversion was thus observed at 80°C, 90°C, and 100°C. Superior catalytic activity at 80°C afforded the resultant three major hydrocarbon-based products: 2-butanol (1.32%), isobutyl alcohol (0.89%), and 3-methyl-1-butanol (0.89%). Such products have important potential as renewable substitutes in diverse industries. Our study highlights the potential of using NiMoO4/rGo as an effective catalyst for bioethanol conversion due to its mesoporous structure, oxygen groups, and high dispersion of active metal oxide. Overall, this study renders $NiMoO_4$/rGo a viable catalyst candidate in sustainable chemical processes and thus accelerates the application of bioethanol to manufacture precious hydrocarbon derivatives. These findings underscore the key to optimizing temperature conditions to maximize product yield and enhance the economic viability of renewable energy resources.

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INTRODUCTION

Pineapple (*Ananas comosus*) is a popular tropical fruit worldwide known for its delicious flavor, distinctive smell, and many health benefits. As a rich source of vitamins A, iron, calcium, sucrose, and mineral constituents, pineapple is commonly found in Indonesian households, and the country is one of the largest producers of this fruit worldwide [1], [2]. Around 20 percent of the fruit is eaten or processed as juice or cooked; the other 80 percent, mostly the skin, is thrown away as organic waste. The composition of high-cellulosic material in this waste creates serious environmental-related problems, leading to pollution and possibly human health issues [3], [4]. Pineapple skin rich in chemicals (cellulose, hemicellulose, and complex carbohydrates) can serve as a promising raw material for industrial utilization [5]. Examples of current applications include it's conversion into bioethanol, vinegar, and other bioenergy products, which exhibit its unutilized potential as a source for sustainable solutions [6], [7].

Upcycling pineapple skin by-products to produce bioethanol is a possible solution to tackle waste management problems and provide high-value-added products. Bioethanol produced from fermentation is also a source of hydrocarbon and butanol derivatives generated by hydrogenation [8], [9]. As alternative solvents and fuel precursors, these derivatives contribute to the sustainable goal of worldwide coal and oil dependency reduction. The availability, low cost, and compliance with zero-waste concepts make pineapple waste economically attractive [10]. Reliable and efficient conversion processes demand advanced catalytic systems that can overcome thermodynamic limitations to fuel hydrogenation reactions under ideal conditions [11]. Heterogeneous catalysts, particularly bimetallic composites, such as Ni-Mo oxides supported on reduced graphene oxide (rGO), have emerged as promising candidates owing to their excellent thermal stability, high active sites, and effective catalytic activity [12].

Ag-based catalytic materials, for instance, underwent significant modifications through the incorporation and optimization of rGO support, improving the atomic economy of catalysis at the molecular level. The hydrothermal method is one of the most conventional methods for preparing these catalysts owing to its relatively straightforward procedures and material properties that can be adjusted [13]. Increasing evidence suggests that Ni-Mo/rGO catalysts function far better than single metals in hydrogenation reactions, making them promising candidates for converting bioethanol to high-value hydrocarbons. Using FTIR, SEM-EDX, XRD, and gas sorption analysis, this paper describes the characterization of the newly prepared $NiMo_4$/rGo catalysts and their performance for the bioconversion of bioethanol. This study adds value to the catalytic conversion of agricultural waste into energy sources characterized by renewability; the pineapples are wasteful and possess the potential for being an excellent feedstock [14], [15].

The heterogeneous catalyst employed for this chemical reaction is in the solid phase, disconnecting the reactants and products in the liquid or gas phase. However, support is very important for the efficiency of these catalysts, as it can improve the dispersion of the active sites and maintain structural stability during the reaction process. The catalytic activity is largely determined by using an appropriate support material that provides more effective exposure of the reactants to the active sites and also assists in refining the reaction process. In recent years, adding a second metal to enhance the catalytic properties has led to the discovery of bimetallic composites as a new generation of catalytic materials. Such composites display unique physical and chemical properties, such as significant thermal stability, lower interaction of the support with active metals, and improved distribution of active species. Drawable properties such as these make bimetallic composites excellent candidates for various catalytic applications. These materials highlight the possibility of achieving stable and effective catalytic activity for energy production and environmental and chemical synthesis [15], [16].

The hydrothermal method is a comparatively facile way of preparing nanoparticles in the aqueous solution under mild temperature and pressure [17]. In a prior research study by Xu et al. [36], NiMo was a promising and innovative metal utilized in a hydrothermal carbonization process, whilst Al_2O_3 was used as a support material to improve the surface area of the catalysts. Moreover, NiMo/rGo was synthesized hydrothermal and applied as the catalyst for low-cost water electrolysis-based hydrogen production. Ni and Mo are present as active sites that have been extensively explored. Metal oxide was used as catalyst support to enhance the optimization of catalyst application and reduce graphene oxide [19], [20].

This work, a development of the previous work, aims to synthesize Ni-Mo oxides supported by rGo as a new catalyst for converting bioethanol from pineapple fruit waste into other hydrocarbon products. Hence, Catalyst was characterized by following Fourier transform infrared (FTIR) spectroscopy (Perkin Elmer Spectrum Version 10.5.1), Gas sorption analyzer (GSA) (Quanthachrome), Scanning electron microscope with Energy dispersive X-ray (SEM-EDX) analysis using (JEOL JED-2300), and X-ray diffraction (XRD) technique (Bruker D2 Phaset Gen). Hydrogenation was conducted to convert bioethanol to a hydrocarbon product with an active catalyst. A gas chromatography-mass spectrometer (GC-MS, Shimadzu QP2010 SE) was used to analyze the conversion products.

METHODS

1. Material

The pineapple skin waste was collected from a local vendor in Yogyakarta, Indonesia. Chemicals such as Yeast Saccharomyces Fermipan, nickel(II) nitrate hexahydrate, Ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}.4H_2O$), potassium hydroxide (KOH), reduced graphene oxide (rGo), and ethanol was purchased from Sigma-Aldrich and used without purification.

2. Preparation of Bioethanol

Room temperature was used to set up all the experiments. The dried pineapple wastes were the pretreatment process. They were washed and disposed of with distilled water and dried with sunlight overnight and in the oven for 48 hours. In the next experiment, powdered dried sample was used through milling. Generally, 2.5 kg of dried pineapple sample was soaked in 1000 mL of distilled water, and 50 g of saccharomyces cerevisiae was added. The mixture was stirred vigorously for 30 min and then hermetically closed to fermentation for 8 days. Then, the product came through filtration, where the supernatant was obtained. A vacuum evaporation process at 65 for 60 min evaporated the filtrate of the resulting fermentation process. GCMS characterized the bioethanol generated.

3. Preparation of $NiMoO_4$/rGO

The $NiMoO_4$/rGO catalyst was explored by earlier work using reduced graphene oxide (rGO) as substrate [21]. Graphene oxide (rGo): 0.5 g, $Ni(NO_3)_2.6H_2O$:

7.2 g, $(NH_4)_6Mo_7O_{24}$: 1.8 g, which were mixed and mixed completely and added PH $4H_2O$ after 100 ml deionized water by thawing at high temperature for 30 minutes. While stirring, the temperature was slowly raised to 60-70ºC, and 2 M sodium hydroxide solution was added dropwise to keep the pH around 8-9. It was then precipitated and collected in a glass beaker. The precipitation was rinsed with deionized water and then subjected to the calcination process carried out in the stainless-steel rector under a nitrogen gas atmosphere for three h at the temperature of 400ºC, then cooled to room temperature; the resultant $NiMoO_4$/rGO catalyst was retrieved for further characterization.

4. Conversion of Bioethanol by Hydrocracking Process

The hydrogen gas cleaned the reactor (boiling flask three necks) with a flow rate of 25 mL/min at 100ºC for 15 minutes. Inside the reactor, a 1.0 g of $NiMoO_4$/rGo catalyst was fixed to a catalyst holder. Afterward, 10 g of bioethanol was injected into the reactor. Under a hydrogen atmosphere, the reactor was heated to 90ºC and 105ºC through a continuous heating process. The GCMS analyzed the yield obtained at every individual temperature.

RESULTS AND DISCUSSION

1. BET Surface Areas, Pore Distributions, and Pore Volume

Hydrogen gas followed by 15 minutes outgassing at 100ºC with a 25 mL/min flow rate was used as a reactor to clean the boiling flask's three necks. Inside the reactor, a 1.0 g $NiMoO_4$/rGo catalyst was installed in a catalyst holder. After that, the reactor was fed with 10 g of bioethanol. The reactor was heated up to the following temperatures: 90ºC and 105ºC, both under a hydrogen atmosphere and with a continuous heating process. The result was collected at each specific temperature and decoded by the GCMS. The nitrogen adsorption-desorption isotherm at 77K of the $NiMoO_4$/rGO catalyst is shown in Figure 1.

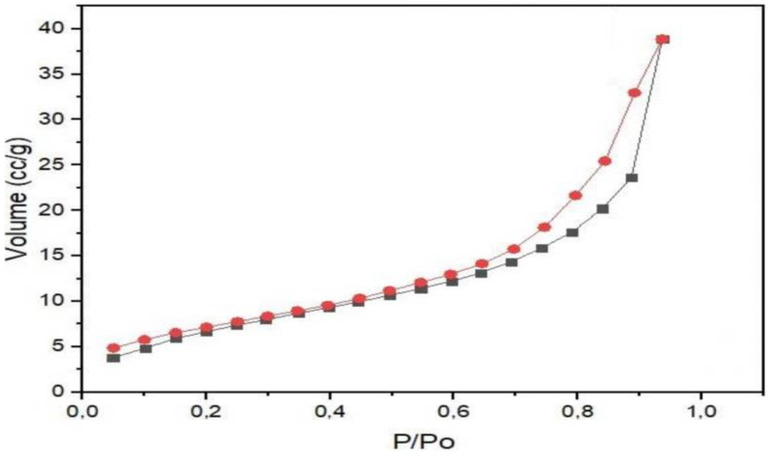


Figure 1. Nitrogen adsorption-desorption isotherm at 77 K of Ni-MoO_4/rGO

The BET method determined the surface area at T/T_o = 0.05–0.3. A hysteresis loop at P/Po >0.4 suggests a typical mesoporous structure. As can be seen from this result, they meet the type II and IV isotherm of the IUPAC Classification with a micro- and mesoporous structure. The results of BET surface area, pore size distribution, and pore volume are listed in Table 1. This data indicates that the adsorbent's pore size distribution compared to the previous observation [22], [23], [24] is highly mesoporous (2-50 nm).

Table 1. BET surface area, Pore size distribution, and Pore volume

BET surface area (m^2/g)	Pore size distribution (nm)	Pore volume (cm^3/g)
26.9	4.5	0.06

2. Characterization of Ni-MO_4/rGo

The FTIR was given in Figure 2 to characterize the functional group in the catalyst. The broad peaks at 3420-3415 cm^{-1} are attributed to the -OH stretching vibration of the hydroxyl group. Two peaks at 2918 cm^{-1} and 2846 cm^{-1} confirmed the C-H group. The peak at 1715 cm^{-1} is associated with the C=O stretching vibration of the carboxyl group. The peak at 1625 cm^{-1} is owing to the C=C stretching of the unreduced graphitic domain. Also, the weak peaks of rGo material at 1372 cm^{-1}, 1220 cm^{-1}, and 1030 cm^{-1} are associated with C=O stretching vibration of carbonyl groups, C-OH stretching of alcohol groups, and C-O stretching vibration of (C-O-C) groups, respectively. The peak at about 828 cm^{-1} corresponds to the asymmetric stretching vibration of the Mo-O and Ni-O linkage. The peaks at about 481cm^{-1} confirm the Ni-O-C and Mo-O-C bond [25], [26]. The outcome of these data corroborated the metal oxide's good distribution onto the rGo surface.

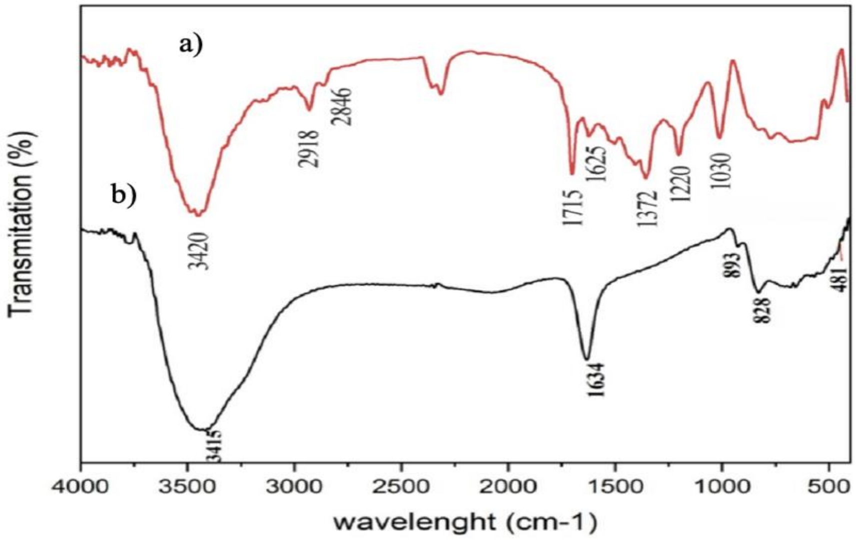


Figure 2. FTIR spectra for (a) rGo and (b) $NiMoO_4$/rGO

3. X-Ray Diffraction Analysis

The XRD results of the $NiMoO_4$/rGO catalyst are illustrated in Figure 3. The characteristic peaks observed at $2\theta < 31.64^{o}$ are attributed to graphite with an amorphous structure of the rGo [27]. The NiO diffraction line appeared at the angles of $2\theta = 37.33^{o}$, 43.24^{o} (220), and 62.46^{o} (221). The MoO3 was observed at $2\theta = 44.48^{o}$, 53.80^{o}, 76.35^{o} which finely matched the standard JCPDS: 00-0120348, JCPDS card 86–0361 and

JCPDS: 00-0040835 [28]. $NiMoO_4$/rGO has a simple cubic structure with an average crystalline size of 49.12 nm. This result indicates that the composite metal oxide was homogeneously loaded on the surface of rGo.

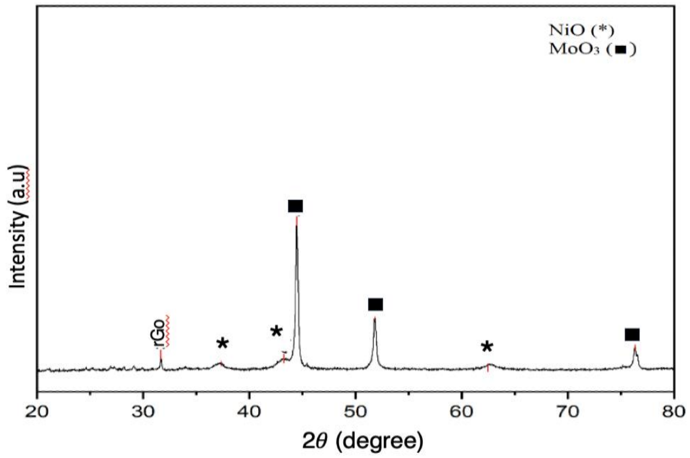


Figure 3. X-ray diffraction spectra of $NiMoO_4$/rGO

4. SEM EDX Analysis

Figure 4 shows the composite's morphology structure and chemical distributions, which the SEM-EDX analyzed. NiMoO4/rGO has a large porosity; its surface morphology is an irregular structure or unsmooth surface. The chemical composition of the composite was confirmed with the help of EDX analysis, which showed nickel (59.96%), Molybdenum (3.75%), carbon (21.28%), sodium (0.49%), and oxygen (14.52%). The use of sodium hydroxide in the precipitation process and the fact that the water is not leached during washing and hydrothermal will contribute to sodium only in the chemical composition. The SEM-EDX mapping results of the rGo surface reveal the dispersal of elements.

This physical agglomeration of elements on the rGo surface can further be evidenced by the scanline of the mapping in Figure 5. The scanline result demonstrates the substantial orange color, a sign of nickel on the highest level of the composite [29]. A particular color was used to depict the distribution of elements. The distribution of metals on the surface is believed to be conducive to the catalyst's active site.

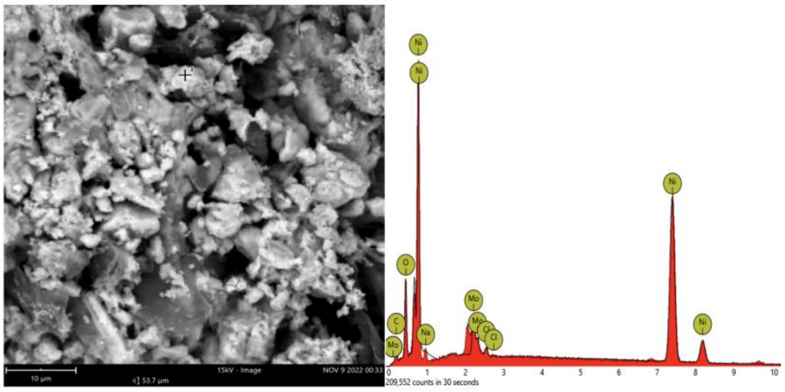


Figure 4. Morphology structure of $NiMoO_4$/rGO

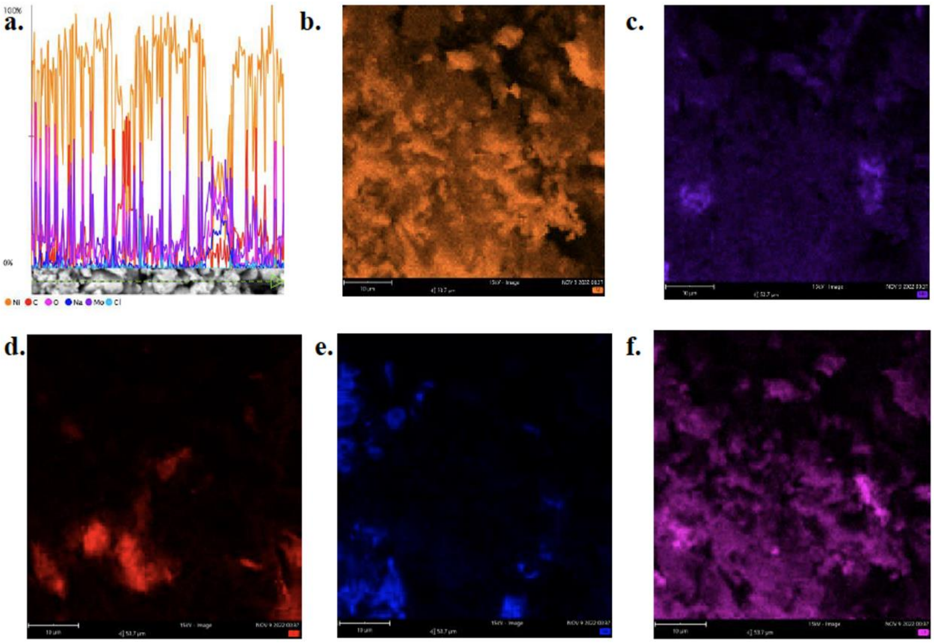


Figure 5. SEM-EDX mapping of distribution metal oxide on the surface of rGo, (a) scanline, (b) nickel, (c) Molybdenum, (d) carbon, (e) sodium, and (f) oxygen

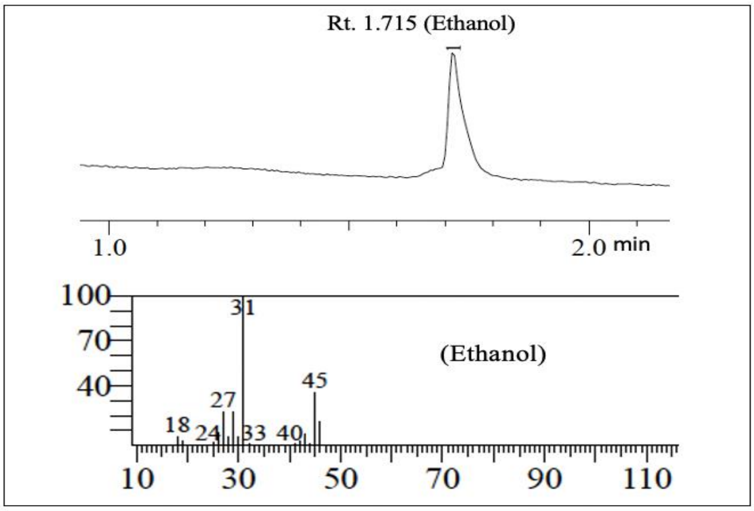
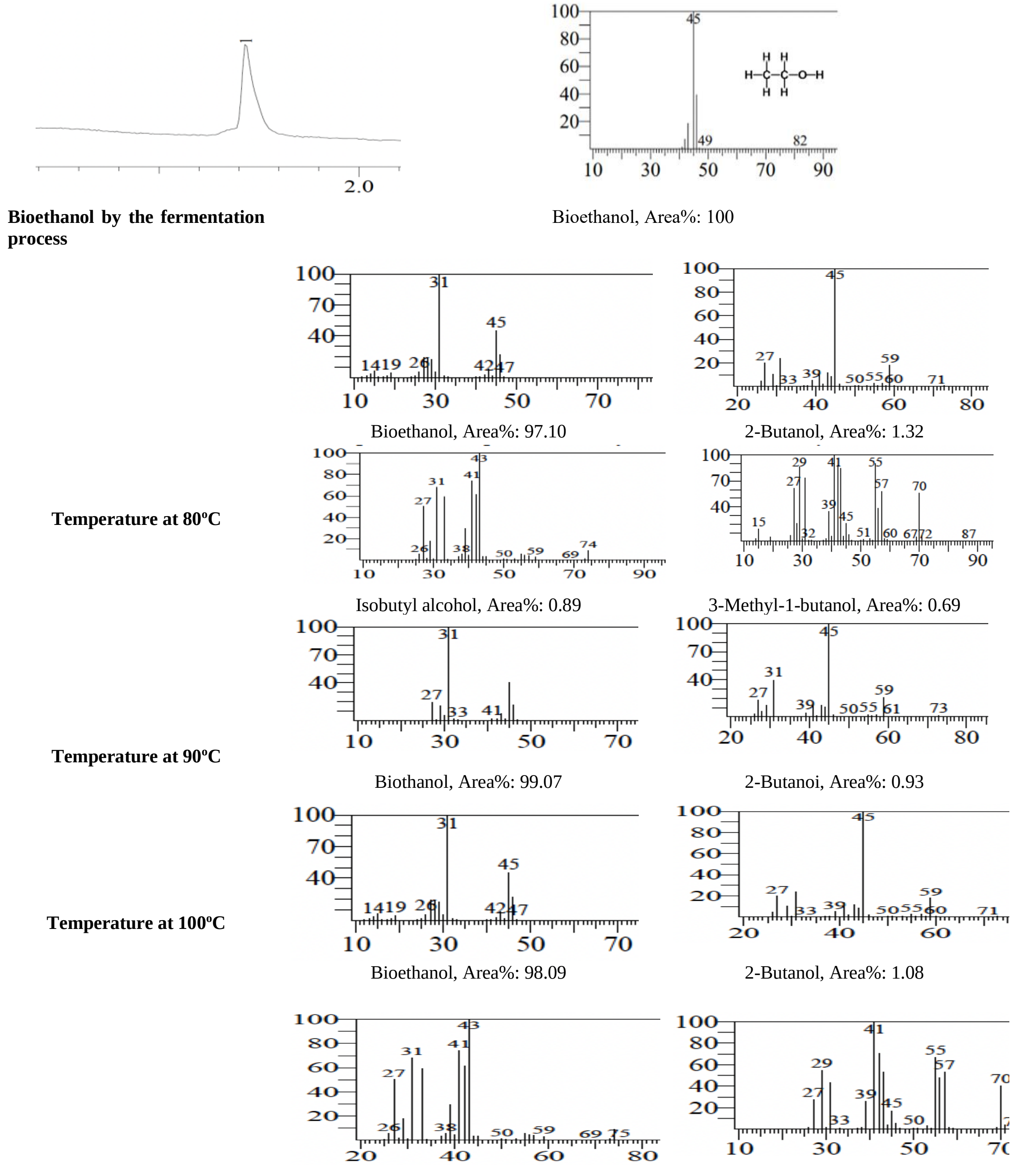


Figure 6. GC-MS spectra of bioethanol from pineapple waste

Table 2. The results of conversion of bioethanol by using $NiMoO_4$/rGO catalyst at different temperatures

Temperature at 80^{o}C	Percentage area (%)	Temperature at 90^{o}C	Percentage area (%)	Temperature at 100^{o}C	Percentage area (%)
Bioethanol	97.10	Bioethanol	99.07	Bioethanol	98.09
2-Butanol	1.32	2-Butanol	0.93	2-Butanol	1.08
Isobutyl alcohol	0.89			Isobutyl alcohol	0.47
3-Methyl-1-butanol	0.69			3-Methyl-1-butanol	0.37

GC Spectra of products | **GC-MS of conversion products**



Bioethanol by the fermentation process

Bioethanol, Area%: 100

Bioethanol, Area%: 97.10

2-Butanol, Area%: 1.32

Temperature at 80ºC

Isobutyl alcohol, Area%: 0.89

3-Methyl-1-butanol, Area%: 0.69

Temperature at 90ºC

Biothanol, Area%: 99.07

2-Butanoi, Area%: 0.93

Temperature at 100ºC

Bioethanol, Area%: 98.09

2-Butanol, Area%: 1.08

Isobutyl alcohol, Area%: 0.47

3-Methyl-1-butanol, Area%: 0.37

Figure 7. GC-MS spectra (a) conversion of bioethanol to other products using catalyst at a temperature of 90ºC, and (b) at a temperature of 105ºC

5. Conversion of Pineapple Waste to Bioethanol

Pineapple waste houses materials like fibbers and volatile compounds with a certain smell. The waste originating from pineapples was widely utilized for bioethanol production by fermentation [30]. The hydrolysis process produced simple sugar from the pineapple waste, which was carried out by fermentation to produce bioethanol products. Bioethanol, a colorless liquid, was identified by Gas chromatography-mass spectrometry (GCMS) (Figure 6). GCMS data showed one peak on the GC as an indication of 100% bioethanol based on the MS analysis.

6. Conversion of Bioethanol to butanol derivates by Catalytic Process

NiMoO4/rGO catalyst converted bioethanol liquid in flowing hydrogen gas at the measured range of temperatures. It is presented in Table 2 as the percentage of the conversion. Product analysis also found hydrocarbon products like kerosene or butanol-derivate products related to previous studies [31]. The butanol-derivates products presented by the GCMS analysis consist of 2-butanol, isobutyl alcohols, and 3-methyl-1-butanol. Note that the fraction of 2-butanol was determined to be 1.32 % and dropped down when the temperature was increased. Why is that so? Because the majority of bioethanol has been converted into products of butanol derivatives at elevated temperatures.

Temperatures were the key operating factors that impacted the conversion process and product distribution. Nevertheless, the conversion of pineapple waste produced the best bioethanol in 1.715 min retention time. The highest product formation is bioethanol, followed by 2-butanol (1.32%), isobutyl alcohol (0.89%), and 3-metyl-1-butanol (0.89%). In contrast, the intermediate process that limited the conversion processes was identified as uncontrolled high temperatures that could release the desired products and the formation of cokes on the active site catalyst.

CONCLUSION

The characterization of NiMoO4/rGo material indicated promising materials as hydrogenation catalysts for their relatively high Brunauer–Emmett–Teller (BET) surface area with a mesopores structure, rich functional groups, nanoparticle sizes, and a good distribution of the elements. The catalyst activity was verified to convert the bioethanol of pineapple waste into hydrocarbon class or butanol-derivate products. The conversion products are 2-butanol, isobutyl alcohol, and 3-metyl-1-butanol. This confirms the NiMoO4/rGo catalytic activity, which has been identified as another promising catalyst in the bioethanol-to-hydrcarbon conversion reaction.

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