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Upgrading of Waste Cooking Oil via Transesterification and Catalytic Hydrotreatment Process

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ABSTRACT

Renewable biofuels, such as biodiesel produced from used cooking oil (WCO), offer an affordable, environmentally friendly alternative to traditional fuels. The main aim of this work is to produce biodiesel from waste cooking oil (WCO), a sustainable alternative to address the challenges associated with renewable energy and resource efficiency. Optimal conditions for biodiesel production were identified, revealing that a 6:1 methanol-to-oil ratio, 1.0 wt.% sodium hydroxide, 60°C, and 60-minute reaction time yielded the highest output in a single-step transesterification process. To enhance the quality of second-generation biodiesel by converting it into more stable hydrocarbon fuels using the hydrodeoxygenation process with the help of MoS2 and NiMoS2 catalysts that were hydrothermally synthesized to demonstrate their effectiveness in improving biodiesel production in the hydrotreatment process. Renewable biodiesel produced through deoxygenation (DO) pathways has a high concentration of linear hydrocarbons(paraffins) and low levels of oxygen and nitrogen. To ensure the quality of the trans-esterified, renewable biodiesel, its properties were analyzed and compared using gas chromatography-mass spectrometry (GC-MS). This paper compares conventional and advanced methods for producing biodiesel, with a focus on the importance of sustainability and efficiency in fuel production.

Keywords: Waste Cooking Oil (WCO), Transesterification, Hydrodeoxygenation, GC-MS analysis, Calorific Value.

1. Introduction

The rising energy requirements driven by industrialization and economic development are primarily met by fossil fuels such as petroleum, coal, and natural gas [1]. However, these are limited resources that take millions of years to form, have few reserves, and are very expensive. The utilization of fossil fuels in internal combustion engines leads to environmental issues, including the expansion of carbon dioxide levels in the atmosphere and the amplification of the Earth's average temperature [2]. The global proportion of renewable energy is anticipated to increase substantially by 2050, reaching 77% by the 1.5°C climate target, according to reports from organizations such as the International Renewable Energy Agency (IRENA). The goal is to enhance energy security, reduce the impact of volatility in fossil fuel prices, and improve affordability by boosting the competitiveness of renewable energy sources. But the shift in emphasis from fossil fuels to eco-fuels is currently problematic due to the lack of sustainable production methods for eco-fuels, despite their ecologically beneficial and renewable nature [3]. Research on biodiesel production from non-edible and waste oils has focused on identifying cost-effective raw materials that don't compete with the food market; waste cooking oil is widely available and helps reduce production costs globally, which comprises mixed vegetables like sunflower, palm, rapeseed, and soya.[4]. Waste cooking oils primarily consist of triglycerides, making up at least 95% of their content, which are formed of long-chain fatty acids, including palmitic acid (C16), stearic acid (C18), oleic acid (C18), lauric acid (C12), etc. [5]. The conversion of waste cooking oil into biodiesel generated interest in its potential as a renewable and sustainable energy source. The transesterification technique is utilized to transform triglycerides into methyl esters, applicable as biodiesel. Hydrotreatment is a method that incorporates the extraction of oxygen from vegetable oils or animal fats to generate hydrocarbon fuels. This process produces fuels with characteristics like petroleum-derived diesel.

1.1 Transesterification

Transesterification of vegetable oils improves the quality of biodiesel by reducing its viscosity and boosting other physicochemical characteristics [6]. The transesterification mechanism involves a nucleophilic attack on the carbonyl carbon of the starting ester of vegetable/plant oil by the incoming alkoxide from the catalyst. This results in the formation of a tetrahedral intermediate, which can either regenerate the starting material or advance to the trans-esterified product and glycerol.

1.2 Hydrotreatment

Utilizing the supported and unsupported catalysts, bio-hydrogenated diesel is produced from WCO with a high acid value (28.7 mg-KOH/g - oil) [7]. The process of hydrotreatment of vegetable oils or animal fats is a highly attractive technique to produce biofuels because it has a favorable carbon mass balance, estimated to be over 95% that exhibits superior quality compared to ester-type biodiesel fuels. Additionally, hydrotreated fuels emit lower levels of CO, NOx, hydrocarbons, and engine smoke than petroleum-based diesel [8]. The presence of hydrogen flow is vital in the hydrotreatment process of feeds due to its dual role as both a reactant and a catalyst surface aid in the

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elimination of water by-products, hence reducing deactivation. Hydrocracking reactions often happen along with hydro-treatment reactions. The process involves the destructive hydrogenation of big molecules, resulting in the breaking of C–C bonds and the formation of lighter products. The process of isomerization also occurs during the subsequent synthesis of hydrocarbons found in gasoline and diesel fuel. To reduce chain polymerization reactions that result in coke deposits on the catalyst surface, it is necessary to use high H2 pressures and relatively high reaction temperatures for these reactions.

1.3 Importance of Catalyst in Biodiesel Production

Hydro-processing is facilitated by group VIII metals like nickel, palladium, and platinum. Additionally, because group VIB metals like molybdenum and tungsten are resistant to oxygen, acids, and alkalis, they have also been utilized in oxygen removal processes [9]. Specific catalysts, such nickel-molybdenum (Ni- Mo)/alumina (Al_2O_3) and cobalt (Co)-Mo/Al_2O_3, are being studied for their potential application in hydrogenation. The utilization of the $NiMoS_2/\gamma$-Al_2O_3 catalyst in the hydrotreating process of palm oil led to product yields exceeding 90%, with an n-alkane concentration above 95.5%. A recent study demonstrated that bimetallic NiW modified ZSM-5 catalysts may achieve a remarkable conversion rate of 96.2% in the hydrogenation process of crude palm oil. The resulting hydrocarbon products include gasoline (C5–10), kerosene (C9–11), and diesel (C10–20) [10]. MoS_2 is essential in hydrotreatment methods for biodiesel production as it acts as a catalyst for the hydrodeoxygenation (HDO) of biodiesel. Transition metals such as nickel (Ni), copper (Cu), zinc (Zn), and iron (Fe) are commonly used catalysts for deoxygenating waste cooking oil model compounds. The unsupported $NiMoS_2$ catalyst showed excellent effectiveness in the hydrodeoxygenation (HDO) process of oleic and palmitic acids, with a conversion level of 95-100%. Additionally, it exhibited a remarkable selectivity for C18 and C16, with percentages of 78.8% and 78.5% respectively, and yielded 70.3% and 65.6% respectively. This study examined the process of hydrodeoxygenation of WCO using MoS_2 and unsupported nickel-molybdenum (Ni- Mo) sulfide catalysts that were produced by a hydrothermal technique.

2. Materials and Methods

2.1 Materials

Used cooking oil was collected from a local restaurant near Shahjalal University of Science and Technology, Sylhet. Chemicals for hydrotreatment process and catalyst synthesis are Thiourea (99%) supplied by Merck Life Science Private Limited (India), Ammonium Molybdate Tetrahydrate (98%) supplied by Sisco Research Laboratories Pvt. Ltd (India), Nickel Nitrate Hexahydrate supplied by Research-Lab Fine Chem Industries (India), n-decane (99%) supplied by Research-Lab Fine Chem Industries (India).

2.2 Catalyst Synthesis

Ammonium Molybdate Tetrahydrate (AMT) served as the precursor for Mo, while Nickel (II) nitrate hexahydrate acted as the nickel source, and thiourea was used for sulfur. To produce MoS_2, 1.0178 g of AMT (98%) and 3.78 g of thiourea (99%) were dissolved in 160 mL of deionized water while gently stirring with a magnetic stirrer. After mixing for 15–20 minutes, HCl (37 wt%) was slowly added to adjust the pH to between 0.8 and 0.9. For the $NiMoS_2$ synthesis, the molar ratio of nickel to molybdenum was kept at 1:2, using 1.15 g of AMT. A different solution was prepared by dissolving 4.25 g of thiourea in 180 mL of deionized water alongside the nickel and AMT precursors. Both solutions were then placed into a 200 mL Teflon liner and set in a stainless-steel autoclave, which was heated to 250 °C for 12 hours. The catalysts were then oven-dried at 60 °C, ground to eliminate solid clumps, and stored in sealed vials. Prior to use, nitrogen gas was introduced into a high-pressure reactor to displace oxygen and enhance catalytic performance. The catalysts were finally annealed for 480 minutes at 330 °C under a hydrogen atmosphere to remove sulfur.

2.3 Characterization

The BET specific surface area of MoS_2 nanosheets was measured using a BET analyzer called ASAP-2020, manufactured by Micromeritics and uses the Harkins & Jura equation to calculate the thickness of multiple layers. The amount of gas adsorbed at each pressure was measured. The BET surface area of bulk MoS_2 and $NiMoS_2$ were determined by analyzing N_2-adsorption isotherms at a temperature of 77 K. By applying the Barrett, Joyner, Halenda (BJH) method to the adsorption branch of the nitrogen adsorption isotherm, mesopore size distributions were estimated. A BET plot was established using data from gas adsorption. The relationship between the relative pressure (P/P_o) range of 0.06-0.3 and the amount of gas absorbed is depicted in the BET plot [11]. A powdered or thin film sample of MoS_2 and $NiMoS_2$ were made. The samples should be carefully powdered to ensure uniformity and reduce the impact of preferred orientations. Usually, a diffractometer is used in XRD analyses. The sample was put on the goniometer stage, which lets it be rotated very precisely. At a certain angle, the X-ray beam was pointed at the sample. The X-rays were bent by the crystal lattice planes of MoS_2 as the sample was turned. The detector recorded the intensity of diffracted X-rays as a function of the diffraction angle (2θ) [12].

2.4 Catalytic Hydrotreatment

The high pressure and high temperature batch autoclave was equipped with a temperature, pressure and stirring controller. For hydrotreating the WCO, waste cooking oil (1.825 g or 10wt% of n-decane), n-decane (25mL), and the catalyst (0.5 g after reduction) were fed into a -mL Parr reactor. The reactor was subsequently purged three times with nitrogen (N_2) and one time with hydrogen (H_2). The system was initially pressurized to 25 bars with hydrogen and then heated to a temperature of 330 °C for 240 min while being continuously stirred at a speed of 100 rpm until it reached the desired temperature. The hydrotreatment process was subsequently carried out for a duration of 8 hours, with a stirring rate of 900 revolutions per minute after reaching the approximate temperature. Following this, the reactor was then cooled to an ambient temperature. After the desired reaction time, the catalyst was separated by filtering to separate the liquid and solid products once the system had cooled to room temperature. The liquid product formed after hydrotreatment, which is rich in n-decane, was defined as catalytic biodiesel in this study. Spent catalysts and char residues were found in the solid residues that were left over after the filtration. After repeatedly washing the solid leftovers with acetone and ethanol to get rid of any remaining n-decane, they were left to dry in an oven for the entire night.

2.5 Product Analysis

1D Gas chromatography (GC) was employed to analyze the liquid product, utilizing a capillary HP-5 column (Max Temp = 330◦C Temp = 330◦C, Length = 30 m, Inner Diameter = 0.25 mm, and film thickness = 0.25 μm) in

conjunction with a flame ionization detector (FID; Shimadzu GC-2030). The carrier gas used in the experiment was helium (He) and it flowed at a rate of 550 mL/min. The sample solution was introduced into the system at a split ratio of 20:1. 1 µL sample was introduced into the gas chromatograph (GC) with the injector and detector temperatures set at 300℃. The oven temperature was programmed to undergo 40℃ at 0 minute then it raised to 70℃ followed by a ramp up to 300℃ at a rate of 15℃ per minute and hold for 5.33 minutes. The total duration counted was 22 minutes. The reaction products were identified using fragmentation patterns obtained from a GCMS-QP2020 NX mass spectrometer (MS) detector and by comparing them to a library of GC products. Each sample was repeatedly injected until the peak area of the desired chemicals reached a consistent level.

3. Results and Discussion

3.1 Optimization of Transesterification Process

The study investigated the impact of varying molar ratios, catalyst quantities, and reaction time on the viscosity of biodiesel produced. The results showed that as the reaction temperature increased, the biodiesel's viscosity decreased, reaching a minimum value of 6.6 mm^2/s. As the reaction temperature rose above the boiling point of ethyl alcohol (64.7°C), the biodiesel's viscosity increased. The optimal temperature for the transesterification reaction was found to be 60°C, resulting in approximately 74% biodiesel production. The study also examined the impact of catalyst percentages on the viscosity of biodiesel at 60°C, with a constant molar ratio (1:6) and reaction time (2 hours). The study found that the reaction did not occur when the catalyst was present in a small proportion, and excessive catalyst concentration decreased the yield of the transesterification reaction and increased the viscosity of the biodiesel. The study concluded that the transesterification reaction may shift towards reactants, causing an increase in biodiesel viscosity.

3.2 Catalyst Characterization

3.2.1 N2 Physisorption Data

The Brunauer-Emmett-Teller (BET) method is used to determine the surface area and porosity of MoS_2 and $NiMoS_2$ catalysts. The BET analysis of N_2 adsorption isotherms is a widely used technique for quantifying the specific surface area of porous materials.

Table 1 displays the precise measurements of the surface area and volume of pores for various catalysts made of sulfide. materials. The introduction of a promoter changes the catalyst's pore structure from type H1 to type H3, indicating that monolayer and multilayer adsorption overlap [13].

The one-step hydrothermal approach produces amorphous MoS2 with a BET surface area of 9.31 m2/g and a pore volume of 0.057 cm3/g. NiMoS2 has a lower surface area and smaller pore volume, with reduced pore size. Both catalysts have type IV isotherms with hysteresis loops typical of mesoporous materials. The introduction of a promoter changes the catalyst's pore structure from type H1 to type H3, indicating that monolayer and multilayer adsorption overlap[13].

3.2.2 Analyze the Result of XRD

The XRD patterns of the prepared MoS_2 and $NiMoS_2$ catalysts reveal a poor crystalline structure, with broad diffraction peaks at 2θ = 15°, 21°, 33◦, and 59°. These peaks correspond to the (0 0 2) and (1 0 2) planes of MoS2, indicating multi-stacked slabs along the c-axis. Sherrer's formula can be used to determine the catalyst's solid size[14].

Table 1. Pore properties of catalysts.

Sample	Single point surface area at P/Po = 0.25	BET Surface Area	Pore Volume	BJH Desorption average pore diameter
MoS_2	11.41 m^2/g	11.97 m^2/g	0.057 cm^3/g	118.318 Å
$NiMoS_2$	8.7803 m^2/g	9.31 m^2/g	0.038 cm^3/g	132.761 Å

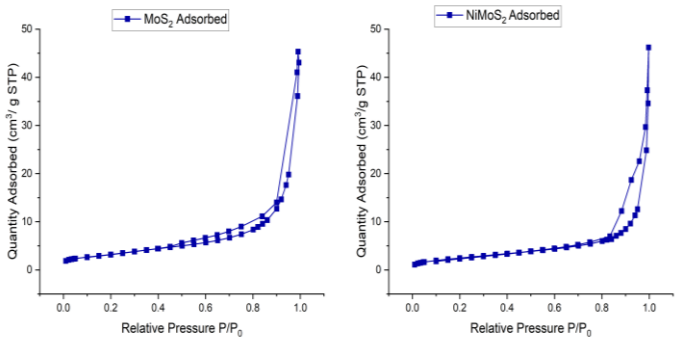

Fig.1: N_2 adsorption–desorption isotherms of the MoS_2 and $NiMoS_2$ catalysts.

The crystalline size of MoS_2 is 6.92 nm, with a crystalline size of 6.92 nm based on the peak with the highest strength. Adding Ni promoter to MoS_2 increases the strength of peaks, potentially aiding in the growth of $NiMoS_2$ crystals. The $NiMoS_2$ catalyst, unsupported, has strong peaks at 2θ =14.4°, 32.8°, 39.5°, 49.5°, and 58.3°, indicating a mix of 1T and 2H MoS_2 phases. The crystalline size of $NiMoS_2$ is 9.07 nm, with a more solid structure compared to the MoS_2 catalyst.

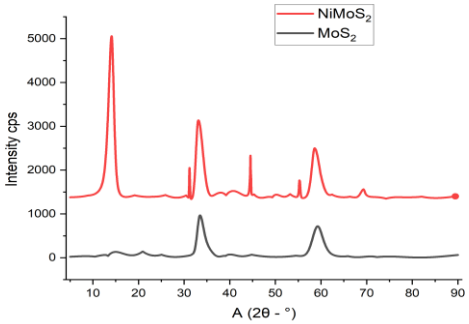

Fig.2: XRD Patterns of MoS_2 & $NiMoS_2$ Catalysts.

3.2 Product Analysis

3.2.1 Analyze the Result of GC-MS

To determine fuel grade, it is crucial to identify the hydrocarbon components present in the hydrotreated product. Three primary reaction pathways extract oxygen from fatty acids to yield alkanes/alkenes: hydrodeoxygenation (HDO), decarbonylation (DCO), and decarboxylation (DCO). The feed (WCO) has a higher proportion of oxygenated components compared to

deoxygenated components, with long-chain fatty acids, specifically C_{18}, in the diesel range[15].

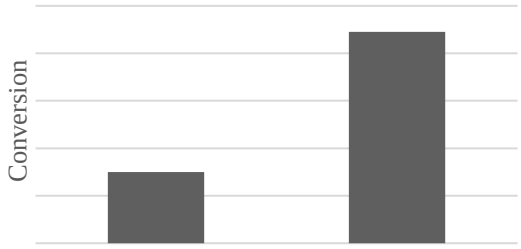

Fig. 3: Conversion of catalytic biodiesel.

The hydrodeoxygenation reaction pathway was found using GC-MS analysis, and the biodiesel conversion yield is greater when using $NiMoS_2$ as a catalyst compared to MoS_2. The desired components in MoS_2 catalyzed biodiesel are alkanes (79.79%), with hydrogenolysis leading to the production of an aldehyde intermediate. The final products consist of paraffins with carbon chain lengths ranging from C_8 to C_{20}, as well as C_{43} from further hydrogenation. The presence of aldehyde intermediates is absent in the $NiMoS_2$ product, indicating its rapid disappearance. The $NiMoS_2$ catalyst exhibits high catalytic effectiveness in the hydrogenation process of straight vegetable oil, resulting in the generation of diesel products (97.70% deoxygenated product).

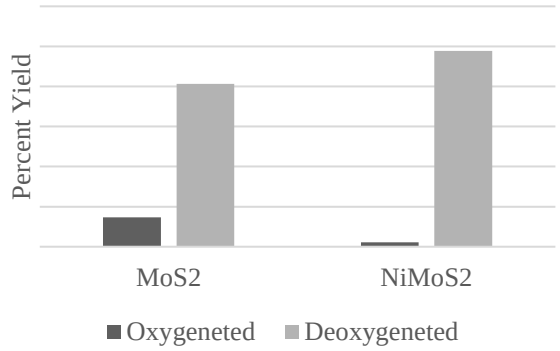

Fig. 4: Selectivity of Oxygenated and Deoxygenated products in MoS_2 and $NiMoS_2$ catalyzed biodiesel respectively.

3.2.2 Comparison of biodiesel via transesterification and hydrotreatment

The GC-MS chromatogram was employed to determine the principal components of the transesterified biodiesel and the resultant product produced with the MoS_2 and $NiMoS_2$ catalysts. Biodiesel mostly consists of methyl esters, whereas catalytic biodiesel contains paraffins (C_8 to C_{20}) within the diesel range. All constituents of transesterified biodiesel contain oxygen (O_2). In contrast, catalyzed biodiesel exhibits a reduced concentration of oxygenated molecules. In the comparison of MoS_2 and $NiMoS_2$-catalyzed biodiesel, the biodiesel catalyzed by $NiMoS_2$ exhibited the lowest concentration of O_2 components. An elevated oxygen concentration in biodiesel may lead to enhanced combustion, although it can also provide difficulties for engine efficiency and design. In such cases, $NiMoS_2$-catalyzed biodiesel is superior to transesterified biodiesel. MoS_2-catalyzed biodiesel ranks as the second most effective option.The production method and catalyst utilized can influence the calorific values of transesterified and catalytic biodiesel. The production of biodiesel utilizing catalysts like MoS_2 and $NiMoS_2$ enhances the process. Transesterified biodiesel possesses a calorific value of around 41.1 MJ/kg, which is somewhat lower than that of normal diesel fuel. The calorific value of catalytic biodiesel is 46.6 MJ/kg with MoS_2 and 49.7 MJ/kg with $NiMoS_2$, surpassing that of conventional diesel and octane.

Table 2. Measured Calorific Value

Biodiesel	**Estimated Calorific Value (HHVs) (MJ/Kg)**
Transesterified Biodiesel	41.1
Hydrotreatment WCO (blank)	To be measured
Hydrotreatment WCO (with MoS_2)	46.6
Hydrotreatment WCO (with $NiMoS_2$)	49.7
Petro Diesel	44.8
Octane 90	41.1

Elevated O_2 content in fuel results in soot production and a reduction in calorific value. The GC-MS analysis indicates that transesterified samples possess a higher oxygen content than catalytic biodiesel. This statement emphasizes the greater efficacy of catalytic biodiesel compared with transesterified biodiesel.

4. Conclusion

The study aimed to determine the optimal conditions for producing biodiesel from waste cooking oil, focusing on the impact of catalyst concentration, reaction temperature, reaction time, and alcohol/oil molar ratio. Sodium hydroxide was used as the catalyst, and the optimal conditions were 60°C, 1 wt% catalyst concentration, and 1:6 oil to alcohol ratio. MoS2 and NiMoS2 catalysts were used to hydro treat biodiesel, producing paraffinic hydrocarbons suitable for diesel engines. The reaction mechanism of catalytic biodiesel was characterized, with the HDO pathway dominating due to higher hydrogen consumption. The study found that catalytic biodiesel produces a higher quality product, while transesterified biodiesel is cost-effective due to its simple production process and availability of raw materials. However, it takes longer to produce compared to transesterification.

5. Ackowledgement

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7. NOMENCLATURE

Symbol	*Meaning*	*Unit*
T	Temperature	(K)
P	Pressure	(Pa)
V	Volume	(m^3)
S_BET	BET surface area	(m^2/g)
d_Pore	Pore diameter	(Å)