HIGHLY THERMAL STABLE CATALYST FOR DEOXYGENATION JATROPHA OIL UNDER FREE HYDROGEN AND SOLVENT FOR HYDROCARBONS LIKE DIESEL FUEL WITH HIGHLY THERMAL FLOW PROPERTIES

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Abstract: Jatropha oil is an oil that obtained from a plant known as Jatropha Curcas. This oil is used as a feedstock due to readily available in nature and will be less expensive compared to another feedstock. In this study, green diesel was produced through deoxygenation of Jatropha oil catalysed by Co15%-La25% bimetallic with activated carbon supported. These activated carbons were obtained through the calcination of the death tree before synthesized it through phosphorylation by mixing it with phosphoric acid for 12 hours at 160 °C before doping it with Lanthanum and Cobalt metal through wet impregnation method. The physico-chemical properties of the prepared catalyst were characterized by using Fourier- transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), thermogravimetric analysis (TGA), gas chromatography flame ionization detector (GC-FID) and gas chromatography mass spectrometry (GC-MS). The effect of catalyst loading, reaction time, and reaction temperature on deoxygenation of Jatropha oil were investigated. The thermal properties from TGA show that the catalyst was stable up to 500 °C. The catalyst demonstrated a superior catalytic performance in deoxygenation reaction under optimal condition (5% catalyst loading, 3 hours and 350 °C), 80 % conversion of Jatropha oil to green diesel was achieved in 3 hours. Reusability test of the catalyst was examined and results showed that the synthesized catalyst could be reused up to 4 times with maintaining Jatropha oil conversion at above 50 %. In nutshell, the Co15%-La25% bimetallic with activated carbon support catalyst is recyclable, reusable and can be used to produced green diesel via deoxygenation of Jatropha oil.

Keywords: Cobalt, deoxygenation, decarboxylation/decarbonylation, green diesel, lanthanum

INTRODUCTION

Currently, fossil fuels are the dominant source for the global energy system. It is expected that fossil fuel will remain as the chief fuel source for the coming 20 years. According to the U.S. Energy Information Administration (EIA), about 80% is derived from fossils fuels, according to the U.S. Energy Information Administration (EIA) (Abdulkareem Ghassan Alsultan et al., 2021; Aziz et al., 2020). Based on current projections, fuel consumption is expected to increase from 95 barrels per day to 113 by the year 2040. Sixty-forty percent of the overall use of fossil fuels is used for transportation, but use is increasing at 0.7% per year. even if rising demand continues, their emissions of greenhouse gases and carbon dioxide range from negative five to negative one kilogram per energy consumption unit (Abdulkareem-Alsultan, Askin-Mijan, Lee, et al., 2016; Abdulkareem Ghassan Alsultan et al., 2021). "The Paris Agreement was signed by 196 nations, including many of the world's major polluting economies, to address the pollution and climate change caused by toxic fossil fuels.” Carbon dioxide production was decreased, but it was still released. Such strict policies would boost the use of renewable and low or zero-carbon-emission fuels to meet human needs. (Islam, Roy, et al., 2021; Shah et al., 2020; Teo et al., 2022). Due to the
uncertainties listed above, as well as the rising cost of fossil fuel, global marketers and energy analysts are looking into alternative sources of energy. In recent years, bio-ethanol or biodiesel from renewable biomass has emerged as a new, viable, and low-cost alternative to fossil fuels (Abdulkareem-Alsultan et al., 2021). Biofuel are organized in three classes: main, advanced, and residual. Second- and third-generation biofuel (Abdulkareem-Alsultan G., Asikin-Mijan N., Lee H.V. et al., 2020). However biodiesel (methyl ester) contents about 11% of oxygen which will make the biodiesel is not stable, thus deoxygenation were used to produce green diesels by fromavieing the oxygen in form of CO and water or CO2 (Abdulkareem-Alsultan et al., 2018; A. Alsultan et al., 2016). In this work Co-La supported catalyst where used to produce green diesel from jatropha oil. The reaction were optimized via one-variable-at-a-time (OVAT).

MATERIALS AND METHOD

This study used jatropha feedstock that has not undergone purification. The crude jatropha characteristics such as the free fatty acid and water content are shown in Table 1. 18.4 % of its weight is made of free fatty acid, which is denoted by TAN at 36.8 mg KOH/g. The content of the jatropha fatty acid comprises of 45.68 % of saturated palmitic, 40.19 % of unsaturated oleic, 7.9 % of linoleic, acid, 4.25 % of stearic and 1.3 % of myristic acid. Sigma Aldrich, a UK based firm supplied anhydrous silver nitrate (Co(NO3)2) with 99.99 % purity. The preparation of AC with prolate shape, functions of surface and high purity characteristics necessitate a two-step process and further treatment of H3PO4. Initially, 1-200 mesh particle sized dried powder date brances (50 grams) was being exposed to pyrolysis within a dinitrogen (N2) atmosphere that is being gradually heated up to 700 °C for 5 hours at 5 °C min-1. A ceramic vertical reactor is used to heat the sample, which was placed within a tube furnace. Concentrated phosphoric acid was used to activate carbonaceous product at a temperature of 158°C for 12 hours. It was then cleaned using hot water with a pH level of 7 and placed overnight in an oven to be dried to create AC. 20 wt. % La(NO3)3.6H2O and 5–30 wt. % Co(NO3)2 were infused into the AC by stirring it continuously for 6 hours. Vacuum impregnating procedure was used to optimise metals impregnation into the support. This process was completed through the use of vacuum machine, Edwards RV12 at 6.3x10–6 mbar. The drying process was completed through the use of rotary evaporator, Stuart RE300DB at a temperature of 55 °C and pressure at -60 kPa for 3 hours. Next, the calcination of AC-doped metals at a temperature of 700 °C within an N2 flow for 4 hours. The following are the composition of AC: Co2O3(1-x)–La2O3x/ACnano, where x=5, 10, 15, 20, 25, and 30 wt. %.

There are several techniques that were used to determine the physicochemical properties of catalyst produced. X-ray diffraction (XRD), Thermogravimetric analysis (TGA), Gas Chromatography with Flame Ionization Detector (GC-FID) and Gas Chromatography Mass Spectrometry (GC-MS) were used to determine the physicochemical properties.

Catalyst preparation

Two-step process and additional treatment with H3PO4 were chosen for the preparation of activated carbons with prolate shape, surface functionality and high purity characteristics. At first, 50g of the dried powder white shell with particle size of 1–200 mesh was subjected to pyrolysis in a N2 atmosphere with heating rate of 5 °C min–1 up to 700 °C for 5 h. The sample was heated in a tube furnace using a ceramic vertical reactor. Carbonaceous product was activated by concentrated phosphoric acid at 158 °C for 12 h, then washed with hot water to pH≈ 7 and further dried in an oven overnight to form activated carbon (AC). The AC was then infused with 20 wt.% Na2O).6H2O and 5–30 wt.% Co(NO3)2 under continuous stirring for a 6 h period. The metals impregnated onto the support underwent optimization with the vacuum impregnating procedure, and this was facilitated with a vacuum machine (Edwards RV12) at 6.3x10–6 mbar. In turn, the Stuart RE300DB rotary evaporator was employed for drying, under the temperature and pressure conditions for a 3 h period amounting to 55 °C and -60 kPa, respectively. Subsequently, AC-doped metals underwent calcination at 700 °C, which lasted for a 4 h period in the context of N2 flow. The name given to the metal-doped AC was as follows: Co2O3(1-x)–La2O3x/ACnano, where x=5, 10, 15, 20, 25, and 30 wt.%.

Catalyst Characterization

There are several techniques that were used to determine the physicochemical properties of catalyst produced. Fourier-transform infrared(FTIR) spectrometry, X-ray diffraction (XRD), Field emission Scanning Electron Microscope (FESEM), Thermogravimetric analysis (TGA), Gas Chromatography with Flame Ionization Detector (GC-FID) and Gas Chromatography Mass Spectrometry (GC-MS) were used to determine the physicochemical properties.

RESULT AND DISCUSSION

physicochemical properties of catalyst
Figure 1 shows that each catalyst produce similar spectrum. All the catalyst produces a broad peak at the range of 2800-3000 cm⁻¹ (Abdulkareem-Alsultan, Asikin-Mijan, & Taufiq-Yap, 2016). This represents the presence of OH functional group in the catalyst. This group comes from the carboxylic acid from carbon support which was treated with phosphoric acid earlier. Other than that, this bimetallic catalyst has a stronger peak at the range of 1700-1710 cm⁻¹ which attributed to the (C=O) stretching mode of the COOH group (Abdulkareem-Alsultan G., Asikin-Mijan N., Lee H.V. et al., 2020). Not only that, (P=O) was found at 1047 cm⁻¹ (Abdulkareem Ghassan et al., 2020). In conjunction, PO stretching vibrations of HPO₄ units as shown in figure, proving the presence of the –PO₂H group covalently bonded to the polyaromatic carbon structure. Finally, the bimetallic catalyst for 5%, 10%, 15%, 20% and 25% shows some moderate peaks at the range of 1650 cm⁻¹ and below which indicates the presence of C=C of the activated carbon support for the catalyst (Faten et al., 2017; Islam, Swaraz, et al., 2021).

Figure 1. FTIR spectrum for bimetallic 5%, 10%, 15%, 20% and 25%

TGA is used to determine the decomposition of compound by observing the change in weight of compound under treatment at increasing temperature (Abdulkareem G. Alsultan et al., 2021; Asikin et al., 2016; Shamil Albazzaz, 2018). Figure 2 shows the TGA profiles for all catalysts. Figure 2 shows that there is small weight loss occur for all the catalyst was similar. Basically weight loss occurs at two different temperatures. Firstly, small weight lost occur at initial temperature for all catalyst due to the loss of adsorbed water in the form of evaporation. The second weight loss for the catalyst occur at range of temperature of 500-600 °C. This weight loss caused by cellulose decomposition (Nurul Asikin-Mijan et al., 2021; Lim et al., 2021; Mansir et al., 2022).

Figure 2. TGA profile of bimetallic supported catalyst under nitrogen heating rate 10°C/min
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Figure 3 shows the XRD pattern for mono metallic Cobalt catalyst with activated carbon support for 5% Co to 25% of Co. it can be said that the XRD diffractogram shows an amorphous structure at around 20= 25° which is typically characteristic of the activated carbon (Lim et al., 2020; Sani et al., 2016). The diffractogram peak appeared was at 20= 7.78 °, 13.86 °, 21.56 ° and 41.78 ° which tally with the XRD diffractogram (JCPDS card file No. 80-1545).

Figure 4 shows XRD pattern for activated carbon and all 15%Co- 5% La, 15% Co- 10% La, 15% Co- 15% La, 15% Co- 20% La and 15% Co- 25% La after calcination at 550 °C for 3 hours. The XRD diffractogram of the AC shows an amorphous structure at around 20 of 25°, which is typical characteristic for activated carbon (Abdulkareem-Alsultan, Asikin-Mijan, Lee, et al., 2016; G. A. Alsultan, Asikin-Mijan, Lee, Albazzaz, Taufiq-Yap, et al., 2017; Muñoz-González et al., 2009). However this structure somehow decrease drastically after the activated carbon impregnated with Co and also La metal solution. Other than that, it also can be seen as the percentage of the La doped in the catalyst increase from 5%- 25%, the intensity of the Co3O4 start to decrease gradually (Abdulkareem Ghassan Alsultan et al., 2022). The low intensity of Co3O4 phases was due to well dispersed of Co3+ into host lattice of mesoporous AC (Abdulkareem Ghassan et al., 2020; Dey & Dhal, 2019; Dietrich et al., 2014). The diffraction peak for Co3O4 at 20= 35.44 ° which represent symmetry plane (JCPDS 78-0431). Meanwhile, the diffraction peak of La was at 20 = 8.46 °, 17.68 °, 25.1 ° and 46.2 ° (JCPDS File No. 01-073-2141) (Abdulkareem-Alsultan et al., 2020a; Nurul Asikin-Mijan et al., 2021).

Figure shows the activated carbon supported before and after treated with phosphoric acid. A random morphology structure was detected in both samples. Before the carbon supported was treated with phosphoric acid, the surface found to be in large, irregular and scattered spores which distributed unevenly. For the carbon support after phosphoric acid treatment, its shows smaller, irregular shape plus there is few agglomerations spotted (Adzahar et al., 2022). Thus, it can be concluded that treatment of phosphoric acid under vacuum can enhance the bond cleavage reaction and H2PO4 ion form hydrogen bonds with the carbon through Grothuss mechanism which increase the surface area of the support (Abdulkareem-Alsultan et al., 2016)/Abdulkareem-Alsultan et al., 2020a).
Highly thermal stable catalyst for deoxygenation jatropha oil under free hydrogen and solvent for hydrocarbons like diesel fuel with highly thermal flow properties

Currently, high performance catalyst are usually made up of material of high surface area. Catalyst performance can be influenced by particle size, shape , and porosity of catalyst. Figure shows the surface particle of catalyst which was calcined at 550 °C were observed to be agglomerated, possibly due to the calcination process (Abdulkareem-Alsultan et al., 2020b). The particles were undefined in shape and the pore of the catalyst was slightly visible. It also can be seen that as the percentage of the lanthanum in the bimetallic catalyst increases from 5% to 25%, the surface of the catalyst become smaller and highly dispersed. Smaller particle size are believed to play an important role to achieve an higher catalytic activity which led to higher dispersion of the Co- La supported carbon catalyst (N. Asikin-Mijan et al., 2022; Ibrahim et al., 2020; Kamil et al., 2020; Shobhana-Gnanaserkhar et al., 2020). The element composition of the prepared catalyst was studied by EDX analysis (Figure 7 and table 2)

Figure 5. FESEM images of activated carbon

Figure 6. FESEM images of bimetallic catalyst
Highly thermal stable catalyst for deoxygenation jatropha oil under free hydrogen and solvent for hydrocarbons like diesel fuel with highly thermal flow properties

**Table 2:** Element composition of the catalyst.

<table>
<thead>
<tr>
<th>CATALYST</th>
<th>ELEMENT COMPOSITION (%)</th>
<th>C</th>
<th>O</th>
<th>P</th>
<th>Co</th>
<th>La</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(15%)-La(5%)/AC</td>
<td>70.12</td>
<td>28.90</td>
<td>0.33</td>
<td>0.03</td>
<td>0.63</td>
<td></td>
</tr>
<tr>
<td>Co(15%)-La(10%)/AC</td>
<td>70.74</td>
<td>24.57</td>
<td>0.82</td>
<td>0.19</td>
<td>3.68</td>
<td></td>
</tr>
<tr>
<td>Co(15%)-La(15%)/AC</td>
<td>71.30</td>
<td>24.49</td>
<td>0.93</td>
<td>0.11</td>
<td>3.17</td>
<td></td>
</tr>
<tr>
<td>Co(15%)-La(20%)/AC</td>
<td>53.56</td>
<td>13.31</td>
<td>0.89</td>
<td>6.84</td>
<td>25.41</td>
<td></td>
</tr>
<tr>
<td>Co(15%)-La(25%)/AC</td>
<td>73.60</td>
<td>23.90</td>
<td>0.69</td>
<td>0.12</td>
<td>1.69</td>
<td></td>
</tr>
</tbody>
</table>

**Selection of catalyst for green diesel production**

For catalyst screening for this project has been done step by step. Firstly a mono metallic cobalt with supported carbon catalyst in the variety of 5%, 10%, 15%, 20% and 25 % of cobalt content was prepared (Aziz et al., 2020). Then all these catalyst was used in deoxygenation process of jatropha oil as feedstock to produce green diesel at 300 °C for 3 hours. The yield produce for each different content of cobalt was calculated (Abdulkareem-Alsultan et al., 2019).

![Figure 7. Percentage yield of green diesel for mono metallic catalyst](image)

From the figure 7 shows that 15% of cobalt supported carbon catalyst produce the highest yield compare to other cobalt catalyst which was 61 %. In order to increase the yield higher, the bimetallic catalyst was planned to prepared. The metal used was lanthanum. The 15% of cobalt catalyst was selected to doped with lanthanum in the range of 15%Co-5% La, 15%Co-10%La, 15% Co- 15% La, 15% Co- 20% La and also 15 % Co- 25 % La with supported carbon respectively. This catalyst is then used for the deoxygenation reaction of jatropha oil at 350 °C for 3 hours. The percentage of yield produced for each percentage of bimetallic catalyst was calculated.

![Figure 8. Percentage yield of green diesel for bimetallic catalyst](image)

Figure 5.0 shows that bimetallic catalyst, 15%Co- 25% La has produced the highest yield at 93 %. Thus, it can be said that 15% Co – 25% La is the most effective catalyst and can be used for the further reaction.
Green Diesel Characterization
The green diesel produced and the properties of the green diesel produced were assessed by using FT-IR and GC-MS. The optimise reaction is at 15% of catalyst loading, 350 °C reaction temperature and also 3 hours of reaction time. Figure 5.1 shows a FTIR analysis carried out to study chemical functional group of Jatropha oil (feedstock) and deoxygenised product. Each spectrum has a wide and strong peak at the range of 2700-3000 cm\(^{-1}\) which belongs to C-H stretching. Absorption band at 1753 cm\(^{-1}\) (C=O) and 1187 cm\(^{-1}\) (C-O) represent the ester group in glycerides and alcohol group respectively which being the main component in the jatropha oil. Therefore, as told by abdulkareem et al., (2017) (G. A. Alsultan, Asikin-Mijan, Lee, Albazzaz, Taufiq-Yap, et al., 2017), the peak intensity appeared in carbonyl group (C=O) and (C-O) in jatropha oil appeared around 1753 cm\(^{-1}\) and 1187 cm\(^{-1}\) can be a measure for the progress of DO reaction. All the deoxygenated oil showed the occurrence of breaking of triglycerides to fatty acid by shifting of C=O (ester) band at 1753 cm\(^{-1}\) to C=O at abruption band of 1730 cm\(^{-1}\) which belongs to the carboxylic acid that is an intermediate product. Besides, the occurrence of DO reaction can be determined by the disappearance of absorption peak at 1187 cm\(^{-1}\) that is belongs to C-O group. The formation of hydrocarbon will not affect the characteristic of C-H stretching peaks at the range of 2700-3000 cm\(^{-1}\) as told by Satyarthi and Srinivas (Satyarthi & Srinivas, 2011).

Optimization of Reaction Parameter
Several parameters were utilized in green diesel production to maximize the production yield. The parameters used are catalyst loading, reaction temperature and also reaction time. Each of the parameter was tested in a broad range to obtain the best parameter for the production of green diesel. Catalyst loading effect the yield of green diesel. In general, as the catalyst loading increases, more active site present hence enhance the production of green diesel. Catalyst loading which are in the range of 0.5%, 1%, 3%, 5% and 7% were tested in reaction at 350 °C for 3 hours. Figure 10 shows effect of catalyst loading on production of green diesel. From 0.5% to 3% of catalyst loading, the yield produced increased gradually but not in a high amount. However, at 5% of catalyst loading, it shows a drastic increase of yield which is 80% of green diesel were produced. Further increase of the catalyst loading to 7% shows a decrease in the yield produced to 22%. The decrease in the yield produced beyond 5% of catalyst loading can be suggested overloading of the catalyst will increase the propensity of secondary reaction and parallel reaction because there is an excess active site for various reactions which will leads to the decrease of the formation of green diesel. Thus, the optimum catalyst loading in this work for deoxygenation reaction is 5%.
Acid catalyst usually required high reaction temperature compare to base catalyst. Hence a series of reaction temperature which are 300 °C, 350 °C, 360 °C and 400 °C were used. The 5% of catalyst loading was used and the reaction time was set up to 3 hours.

Figure 11 shows that green diesel production increases from 300 °C to 350 °C. In general, as the temperature of reaction increase, the kinetic energy of reactant molecule increases where there will be more effective collision thus high production of green diesel. The highest yield of green diesel produced was at 350 °C. Beyond that, the yield produced start to decrease drastically at 360 °C and there is no yield at all at 400 °C.

This phenomenon may be interpreted as an increase in temperature boosting the rate of DO reaction via deCOx pathways to the point where catalyst particles are extensively dispersed in the high viscosed liquid phase, increasing the effective mass transfer of the reaction contents. Increased temperature, on the other hand, led in a drop in DO activity and a decrease in straight chain hydrocarbon output. The high temperature may have boosted the occurrence of alternate cracking reaction pathways, resulting in the formation of lighter fractions (gaseous product) and a drop in liquid hydrocarbon yield. As a result, the best temperature for carrying out the deoxygenation operation is 350 degrees Celsius.

Reaction time at 0.5 hours, 1 hours, 3 hours and 5 hours were used to determine the best time of reaction with temperature at 350 °C and catalyst loading of 5%. Figure 12 shows the trend of yield produced when the reaction time were varied. Starting from the 30 th minutes of the reaction, the yield produced was very low and increase gradually to the maximum yield at 3 hours which was 80% of yield were produced. It shows that as the reaction time increases, the higher DO activity via deCOx pathways by increasing the ability of the reactant molecules to sufficiently react with the catalyst surface. However, beyond 3 hours of the reaction time it shows a drastic decrease in the yield produced. The reason might be due to cracking of oxygenated liquid product into lighter fractions and lead to formation of gaseous products (G. A. Alsultan, Asikin-Mijan, Lee, Albazzaz, & Taufiq-Yap, 2017). Thus, the optimum reaction time for the deoxygenation reaction to produce green diesel is 3 hours.

**Figure 11: Effect of reaction temperature on deoxygenation of green diesel**

**Figure 12. Effect of the reaction time on production of green diesel**

**Reusability of The Catalyst**

Reusability test for catalyst was carried out at optimal conditions. The optimal condition was 5% of catalyst loading, reaction temperature at 350 °C and the reaction time about 3 hours. After the first use, catalyst was separated between liquid products by filtration. Then, the catalyst was washed with methanol and dried in the oven for 1 hour to remove excess methanol.
Highly thermal stable catalyst for deoxygenation jatropha oil under free hydrogen and solvent for hydrocarbons like diesel fuel with highly thermal flow properties

Figure 13. Reusability test of 15% Co-25% La catalyst

Figure 13 shows the result of reusability test. Reusability of catalyst was only carried out by using 15% Co – 25% La over carbon supported catalyst. For the first trial the green diesel production was about 80% but it decreases after reused for the next reaction due to deactivation of catalyst. In addition, deposition of coke onto the surface of the catalyst causes fouling of catalyst. This deactivation also was probably due to the structural changes. The last cycle of reusability obtained was about 49% of green diesel. The cold thermal properties and thermal flow of green fuel was with in the range of the American and British standards confirm that the fuel can be used in the diesel engine with out any issues as showing in table 3

Table 3: fuel properties and thermal cold flow

<table>
<thead>
<tr>
<th>Fuel Properties</th>
<th>EN-14214</th>
<th>ASTM-D6751</th>
<th>Petro diesel</th>
<th>FAME Biodiesel</th>
<th>Green Diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (40°C) CST</td>
<td>3.5-5.00</td>
<td>1.9-6.0</td>
<td>2.71</td>
<td>3.89-7.90</td>
<td>2.5-4.15</td>
</tr>
<tr>
<td>Cloud Point/°C</td>
<td>-</td>
<td>-23-44</td>
<td>-5-15</td>
<td>-25-(-5)</td>
<td></td>
</tr>
<tr>
<td>Pour Point/°C</td>
<td>NA</td>
<td>NA</td>
<td>-21</td>
<td>(-15)-16</td>
<td>(-9)-16</td>
</tr>
<tr>
<td>Flash Point/°C</td>
<td>120 min</td>
<td>130 min</td>
<td>52-136</td>
<td>96-188</td>
<td>90-134</td>
</tr>
</tbody>
</table>

CONCLUSION

The Co-La supported carbon catalyst was produced by doping cobalt and lanthanum together through wet impregnation method followed by calcination. The catalyst undergoes for catalyst screening such as percentage of cobalt and lanthanum content to obtain the highest yield of green diesel. The best catalyst chosen was 15% Co-25% La supported activated carbon which was reflux with phosphoric acid for 12 hours exhibited superior catalytic performance in conversion of jatropha oil to green diesel. Jatropha oil become a suitable feedstock since it is easily available, cheap and environmentally friendly. The catalyst demonstrated a superior catalytic performance in deoxygenation reaction, under the optimal condition which is 5% catalyst loading, 350 °C reaction temperature and 3 hours of reaction time. 80% of conversion was achieved in 3 hours. Reusability test of the carbon-based catalyst was examined and results showed that the synthesized catalyst can be reused up to 4 times with maintaining conversion at above 50%.

AUTHOR CONTRIBUTION

All authors have contributed equally in data collection, study design, data analysis, results, tables, and manuscript preparation.

Conflict of interest: There is no conflict of interest

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