

## Sequential Condensation and Hydrodeoxygenation Reaction of Furfural-Acetone Adduct over Mix Catalysts Ni/SiO<sub>2</sub> and Cu/SiO<sub>2</sub> in Water

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### ABSTRACT

Sequential condensation and hydrodeoxygenation reaction were performed using autoclave batch reactor in the presence of water as a solvent. The condensation of furfural and acetone was performed using MgO catalyst followed by hydrodeoxygenation using mix catalyst Ni/SiO<sub>2</sub> and Cu/SiO<sub>2</sub>. The catalyst was prepared by wet-impregnation method and analyzed by XRD, SEM-EDX as well as BET surface. Condensation of furfural and acetone in 1:2 mol ratio was carried out by reflux gave 4-(2-furyl)-3-buten-2-one and 1,5-bis-(2-furanyl)-1,4-pentadien-3-one. The condensation product was then subjected for hydrodeoxygenation using batch reactor, catalyzed by mixed Ni/SiO<sub>2</sub> and Cu/SiO<sub>2</sub> at 150 and 180 °C for 2 h. The product identified as alkane derivatives with the conversion at 38.83 and 50.35%, respectively. The selectivity of hydrocarbon is 61.39% at 150 °C and 16.55% at 180 °C. Increasing the reaction temperature to 200 °C did not give any products except the recovery of the precursor. It showed that higher temperature enhanced the catalyst activity but the selectivity is controlled by low reaction temperature.

**Keywords:** hydrodeoxygenation; furfural; condensation; catalyst; liquid phase

### ABSTRAK

Reaksi kondensasi dan hidroleoksisgenasi dilakukan menggunakan reaktor autoklaf dengan sistem batch dalam pelarut air. Pertama, dilakukan reaksi kondensasi antara furfural dan aseton menggunakan katalis MgO diikuti dengan reaksi hidroleoksisgenasi menggunakan katalis campuran Ni/SiO<sub>2</sub> dan Cu/SiO<sub>2</sub>. Katalis Ni/SiO<sub>2</sub> dan Cu/SiO<sub>2</sub> disiapkan dengan metode impregnasi basah, dianalisis dengan XRD, SEM-EDX, dan luas area BET. Reaksi kondensasi furfural dan aseton dengan perbandingan rasio mol 1:2 dilakukan dengan metode refluks menghasilkan 4-(2-furil)-3-buten-2-on dan 1,5-bis-(2-furanil)-1,4-pentadien-3-on. Produk campuran ini kemudian digunakan sebagai bahan dasar reaksi hidroleoksisgenasi. Reaksi dilakukan pada temperatur 150 dan 180 °C selama 2 jam. Produk yang dihasilkan adalah turunan alkana dengan konversi masing-masing adalah 38,83 dan 50,35%. Selektivitas produk hidrokarbon yang terbentuk adalah 61,39% pada temperatur 150 °C dan 16,55% pada 180 °C. Peningkatan reaksi pada temperatur 200 °C tidak memberikan produk alkana yang diharapkan. Hasil yang didapatkan menunjukkan bahwa peningkatan temperatur reaksi meningkatkan jumlah produk tetapi selektivitas produk ditentukan oleh suhu reaksi yang lebih rendah.

**Kata Kunci:** hidroleoksisgenasi; furfural; kondensasi; katalis heterogen; fase cair

### INTRODUCTION

Catalytic conversion of biomass become attracted world's attention to resolve environment problem and energy demand. The abundant biomass from agricultural waste can be converted to bio-based-chemicals by triple dehydration and hydrolysis into furfural. This compound is a suitable precursor for the production of high quality diesel through sequential condensation and hydrodeoxygenation (HDO) reaction [1].

The HDO reaction is mainly studied using a noble metal such as Pt/C, Ru/C, Pt/C, Rh/C, Pd/SiO<sub>2</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> as catalysts. Zhao (2011) reported the HDO of

phenols to cycloalkanes using Pd/C in the acid medium [2]. Lee (2016) was also reported the HDO of guaiacol using Pt/HZSM converted to cyclohexane [3]. The used of non-noble metal catalyst, such as Ni, Cu and Fe supported on SiO<sub>2</sub> was mainly reported for hydrogenolysis [4-5], pyrolysis reaction [6] and methane decomposition [7]. In my knowledge, there is a limited publication using Ni/SiO<sub>2</sub> or Cu/SiO<sub>2</sub> catalyst for HDO in liquid phase except the used of Ni-Cu/SiO<sub>2</sub> alloy reacted at high temperature and high pressure [1,8]. In accordance with HDO reaction, our group has been reported the HDO of furfurylidene acetone using Ni/Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> gave tridecane (C13) as diesel fraction

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[9]. However, Chen et al. (2014) reported that HDO reaction of furfural derivatives using Ni-Cu/SiO<sub>2</sub> alloy gave alkane compound (C9 and C10) in the various ratio [1]. The higher Ni ratio on the alloy exhibit the best activity [8].

Here, in this research we reported the HDO reaction of furfural-adduct product using mixed Ni/SiO<sub>2</sub>-Cu/SiO<sub>2</sub> catalyst in various reaction temperature to enhance catalyst selectivity over C8 and C13 by sequential reaction. The physicochemical properties of catalyst were fully characterized.

## EXPERIMENTAL SECTION

### Materials

The materials that were used in this research, there are, furfuraldehyde (Sigma Aldrich) in 98% purity and used without distillation, Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O (Merck), Cu(NO<sub>3</sub>)<sub>2</sub>•3H<sub>2</sub>O (Merck), SiO<sub>2</sub> (Merck), Na<sub>2</sub>SO<sub>4</sub> (Merck), aqua demineralized (Hydrobat), dichloromethane, n-hexane, ethyl acetate, and MgO in technical grade supplied by local vendor. Nitrogen (N<sub>2</sub>) and hydrogen (H<sub>2</sub>) gas for calcination and reduction the catalysts were obtained from Samator in UHP grade.

### Instrumentation

The instrument that used in this research were X-Ray Diffraction (XRD) X'Pert Graphics and Identify Philips Analytical, Scanning Electron Microscopy (SEM) Carl ZEISS EVO MA10, spectrophotometer UV-Vis double beam Shimadzu 1600 Series, Spectrophotometer FT-IR Shimadzu 8400S, and GCMS QP2010S with FID detector and 30 m HP 5MS column. Total surface area, pore size distribution, and total pore volume were measured using Quantachrome NOVA 1200. Total surface area was calculated by BET equation and pore size distribution and volume were performed by BJH method.

### Procedure

#### Synthesis of Ni/SiO<sub>2</sub> and Cu/SiO<sub>2</sub> catalysts

The catalyst Ni/SiO<sub>2</sub> was prepared according to Zaccheria method with modification [10]. Nickel loading is prepared for 20% by diluted 9.91 g of Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O salt in demineralized water then stirred until homogenous solution is formed. The solution of nickel salt then precipitated by addition of NH<sub>4</sub>OH solution until pH 9 to form Ni(OH)<sub>2</sub>. SiO<sub>2</sub> (8 g) was added into solution and stirred for 24 h at room temperature. After the solid formed, then dried in oven for 120 °C for a night, calcined at 500 °C for 4 h with N<sub>2</sub> gas flowing. The

catalyst was reduced at 550 °C for 2 h using H<sub>2</sub> gas. The Ni/SiO<sub>2</sub> catalyst was obtained in 8.25 g.

The catalyst Cu/SiO<sub>2</sub> was prepared in similar procedure with previous. The Cu(NO<sub>3</sub>)<sub>2</sub>•3H<sub>2</sub>O (7.6 g) was diluted in water, added with NH<sub>4</sub>OH until pH 9 then added with 8 g of SiO<sub>2</sub> powder. The solution was stirred at room temperature for 24 h. After finished, the solid dried in oven for a night, calcined at 350 °C for 4 h and reduced at 270 °C [10]. The Cu/SiO<sub>2</sub> catalyst was collected in 8.11 g.

All the catalysts were characterized by X-Ray diffraction to analyze the crystallinity, Scanning Electron Microscopy (SEM) connected with EDX to determine the metal content and N<sub>2</sub> adsorption using Quantachrome NOVA 1200.

#### Sequential condensation and hydrodeoxygenation (HDO) reaction

The condensation reaction was performed according Ulfa methods with modification [11]. The reaction was carried out by reflux using furfural and acetone 1:2 mol ratio. Prior to reaction, 0.4 g MgO as a catalyst was activated by heating the solid in tree-neck round bottom flask at 100 °C for 1 h. After activation, 1.16 g furfural (1 mL, 0.012 mol) and 1.8 mL acetone (0.024 mol) put in to flask and added with 40 mL aqua demineralized water as a solvent. The reflux was conducted for 6 h with continue stirring. The condensation product was collected by filtration to separate the catalyst.

The hydrodeoxygenation (HDO) reaction was initialized by activated the mix-catalysts 0.02 g Ni/SiO<sub>2</sub> and 0.02 g Cu/SiO<sub>2</sub> by heating in the batch reactor for 1 h under H<sub>2</sub> gas at ambient temperature. After the reactor is cooling down, the HDO started by inserting the condensation product from the previous step into the reactor then purged with an H<sub>2</sub> gas and heated for 24 h at various temperature. The HDO method used in this reaction according to Ulfa group method with some modification [9]. The reaction temperature applied was at 150 and 180 °C for 2 h. The products from these reactions were then analyzed by Fourier Transform IR and Gas Chromatography.

## RESULT AND DISCUSSION

### Characterization of Ni/SiO<sub>2</sub> and Cu/SiO<sub>2</sub>

The crystal structure of Ni/SiO<sub>2</sub> and Cu/SiO<sub>2</sub> were recorded on powder X-Ray Diffraction (XRD) using Cu-K $\alpha$  radiation at  $\lambda = 1.5406 \text{ \AA}$  scan at  $2\theta = 20-80^\circ$  with scan rate  $1^\circ/\text{min}$ . Fig. 1 showed the XRD pattern of crystalline SiO<sub>2</sub> as support material compared with the catalysts Ni/SiO<sub>2</sub> and Cu/SiO<sub>2</sub> (20% metal loading). The crystalline structure of SiO<sub>2</sub> were detected by the

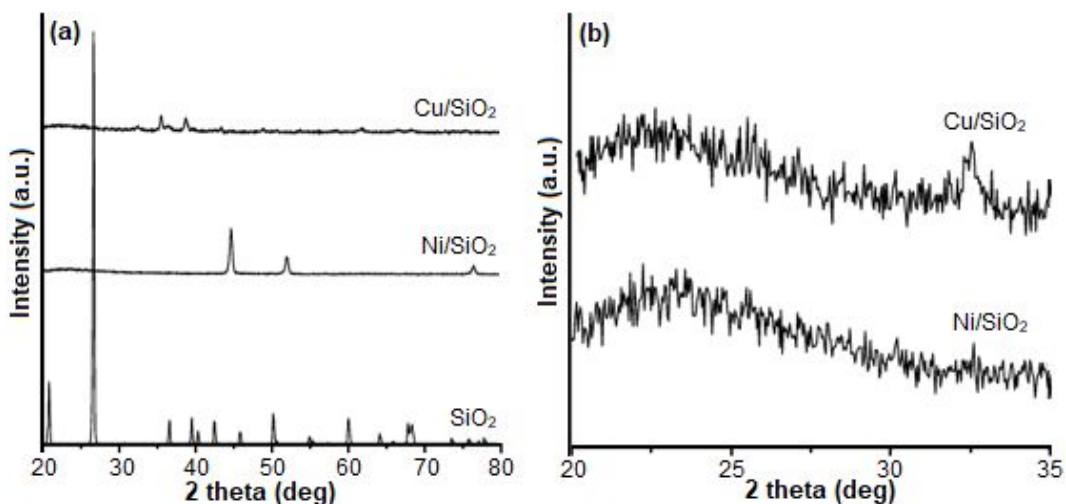


Fig 1. XRD pattern of (a) Ni/SiO<sub>2</sub> and Cu/SiO<sub>2</sub> compared with SiO<sub>2</sub>; (b) amorphous silica profile

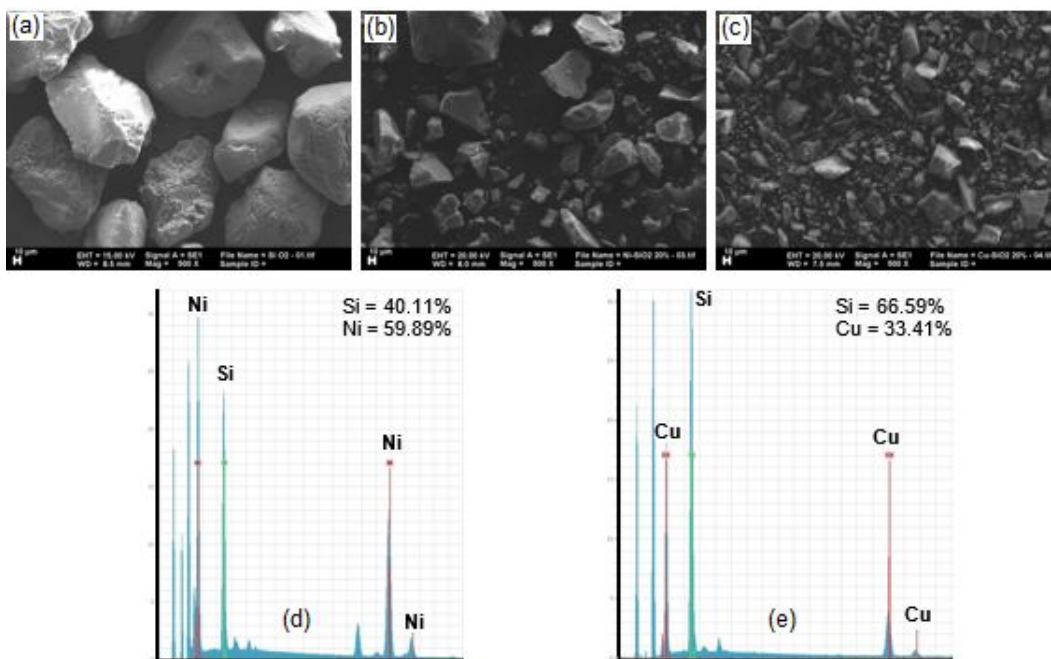


Fig 2. SEM micrographs of (a) SiO<sub>2</sub>; (b) Ni/SiO<sub>2</sub>; (c) Cu/SiO<sub>2</sub> calcined at 350 °C; (d) EDX spectra of Ni/SiO<sub>2</sub>; (e) EDX spectra of Cu/SiO<sub>2</sub>

sharp diffraction of silica at 20.9, 26.7, 39.5, 50.2, and 60.1° (Fig. 1a). However, the absence of crystalline diffraction after Ni and Cu deposition showed that silica was changing to amorphous. The large hump (broad peak) at around 22–30° (Fig. 1b) showed the low degree crystallinity of SiO<sub>2</sub> by the formation of physical interaction between silica and metal [12-13]. Changing the crystallinity of SiO<sub>2</sub> to amorphous after deposition of the metal increased the acidic surface of the catalyst and then enhance the catalytic activity [14].

The profile of Ni/SiO<sub>2</sub> catalyst (Fig.1a, middle) showed particular peaks at 2θ values of 44.56, 51.96,

and 76.51° correspond to Ni(111), Ni(200), and Ni(202) reported by JCPDS no 96-210-0662 [15]. On the other hand, NiO diffractions at 38(111), 44(200), 63(220), 76(222), and 79(311) was not detected. Its means that reduction of catalyst at 550 °C for 2 h followed by H<sub>2</sub> purge completely reduced Ni<sup>2+</sup> into Ni<sup>0</sup> [16].

Fig. 1a (upper) present the XRD patterns of Cu/SiO<sub>2</sub> catalyst after reduced at 270 °C which exhibit diffraction of Cu(111) at 2θ = 44.29° in weak intensity. The main peak of CuO at 2θ = 35.56 and 38.62° were still clearly detected even the reduction temperature is higher than 250 °C [17]. Generally, small particle of CuO

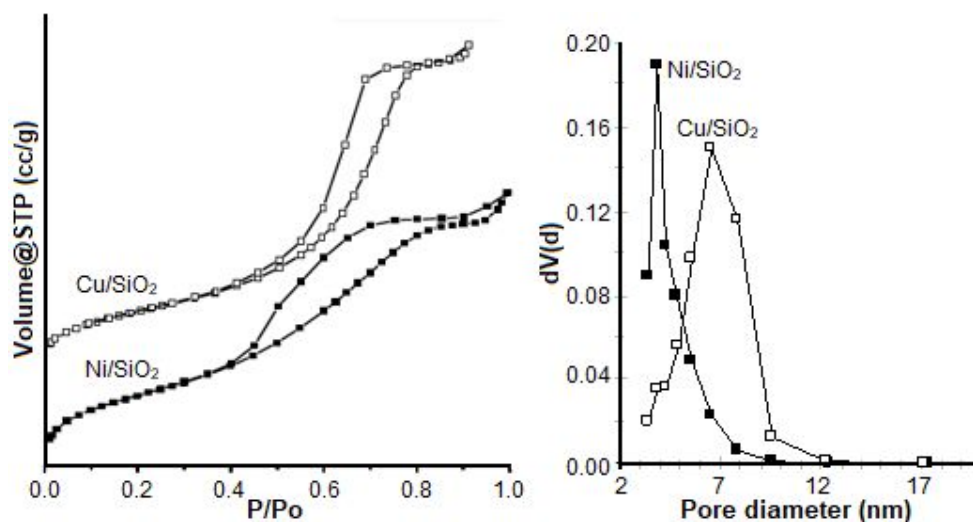


Fig 3. (a) Adsorption-desorption isotherm; (b) pore sizes distribution of catalyst

Table 1. Surface and porous properties of catalysts

Catalyst	Metal content (wt.%)	$S_{BET}^1$ ( $m^2g^{-1}$ )	$V_{meso}^2$ ( $cm^3g^{-1}$ )	$V_{micro}^3$ ( $cm^3g^{-1}$ )	$D_{meso}^2$ (nm)	$D_{micro}^4$ (nm)
Ni/SiO <sub>2</sub>	20	271.2	0.330	0.121	3.840	0.432
Cu/SiO <sub>2</sub>	20	254.4	0.553	0.112	6.601	0.432

<sup>1</sup> $S_{BET}$  (surface area) BET method

<sup>2</sup> $V_{meso}$  (volume mesoporous),  $D_{meso}$  (diameter mesoporous) BJH method

<sup>3</sup> $V_{micro}$  (volume microporous) SF method

<sup>4</sup> $D_{micro}$  (diameter microporous) HK method

have a low reduction temperature. However, this catalyst suggested to have a large particle size (bulk CuO) and low dispersion system made the increasing of reduction temperature. Only small amount of Cu<sup>2+</sup> or Cu<sup>+</sup> is reduced to Cu<sup>0</sup> resulted the low intensity of Cu diffraction [18].

The surface morphology and dispersion of Ni and Cu over SiO<sub>2</sub> support were investigated by SEM. The representative electron micrographs of the catalysts are presented in Fig. 2. The particle size of SiO<sub>2</sub> (~160  $\mu m$ ) is larger than Ni/SiO<sub>2</sub> and Cu/SiO<sub>2</sub> (Fig. 2a). Deposition of Ni and Cu into the surface severely decreased the particle size to ~10  $\mu m$  by the physical interaction between SiO<sub>2</sub> cage with metal. Among the three catalysts, the Cu/SiO<sub>2</sub> exhibit the smallest particle size compared with Ni/SiO<sub>2</sub> and SiO<sub>2</sub> (Fig. 2b-c). To get the information about surface composition element, the energy dispersive X-ray analysis (EDX) was also performed (Fig. 2d-e). As expected, the EDX result revealed the presence of Si, Ni, Cu and O element in appropriate proportions. The deposition of Ni on the surface is higher compared with Cu even the loading of the metal experimentally same. This phenomenon is explained by the faster time nucleation of Ni metal on to the amorphous SiO<sub>2</sub> by 10<sup>3</sup> times compared with Cu [19]. However, the low disperse metal distribution is recorded in EDX which due to sintering process [5].

N<sub>2</sub> adsorption-desorption isotherms of the fresh catalysts are shown in Fig. 3. It was observed that the isotherm trend of Ni/SiO<sub>2</sub> and Cu/SiO<sub>2</sub> followed type IV, the characteristic of mesoporous material with the hysteresis loop at P/Po = 0.4–0.8. Based on the classification of hysteresis curved by de Boer explained in Lowell et al., Ni/SiO<sub>2</sub> have hysteresis type H2 which mean the materials are often disordered, have not well defined distribution of pore size and shape, that is indicated as bottle-neck constriction [20]. On the other hand, Cu/SiO<sub>2</sub> have ordered cylindrical-like pore channels and agglomerates in uniform spheres. This type of hysteresis is classified as type H1 porous materials. The difference of hysteresis type may be associated with pore size distribution, pore geometry, and connectivity of mesoporous material.

Pore size distribution of Ni/SiO<sub>2</sub> and Cu/SiO<sub>2</sub> displayed in Fig. 3b. In accordance with the previous analysis, Cu/SiO<sub>2</sub> have a large pore size ~7 nm with convergent distribution from 3–10 nm. Average pore size of Ni/SiO<sub>2</sub> was smaller might suggest shrinkage in pores during calcination and reduction process [12].

The BET surface area ( $S_{BET}$ ) and porous structure of Ni/SiO<sub>2</sub> and Cu/SiO<sub>2</sub> is tabulated in Table 1. From Table 1, Ni/SiO<sub>2</sub> catalyst have a higher surface area than Cu/SiO<sub>2</sub> which may be caused by the optimum calcination temperature of Ni catalyst. As reported by

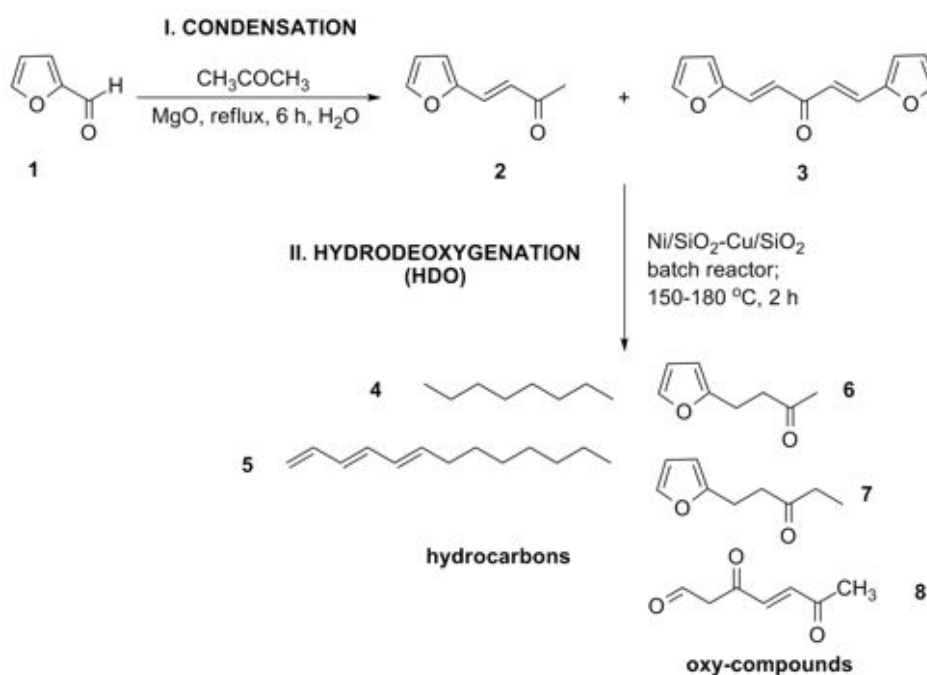
Blanco et al. (2012), calcination temperature at 500–550 °C is optimum condition for calcined and reduced Ni<sup>2+</sup> become Ni<sup>0</sup> deposited on SiO<sub>2</sub> [12]. This data is supported by XRD analysis showed the sharp diffraction of Ni metal. Compared with the reported data by Ulfa et al. (2017) according to the synthesis of Cu/γ-Al<sub>2</sub>O<sub>3</sub> catalysts by wet-impregnation method, the total S<sub>BET</sub> of Cu/SiO<sub>2</sub> have a higher surface area than the subjected catalyst [9]. It is clearly explained that physical properties of the support have a high impact to determine the total surface area. Porosity of the catalyst can be determined by volume (V<sub>meso</sub>) and diameter mesoporous (D<sub>meso</sub>). In overall, V<sub>meso</sub> and D<sub>meso</sub> of Cu/SiO<sub>2</sub> is larger than Ni/SiO<sub>2</sub>. We considered that hysteresis loop of Cu/SiO<sub>2</sub> which have ordered metal dispersion made the catalyst have a higher porosity than Ni/SiO<sub>2</sub>.

### Sequential Condensation and Hydrodeoxygenation (HDO) Reaction

Sequential condensation and hydrodeoxygenation (HDO) performed in this research is as follows. The condensation reaction of furfural (**1**) (λ<sub>max</sub> 270 nm, in MeOH) and acetone (1:2 mol ratio) is carried out using MgO base catalyst followed by HDO of the products using mixed catalyst Ni/SiO<sub>2</sub>-Cu/SiO<sub>2</sub>. The reaction is illustrated in Scheme 1. The condensation was performed by reflux for 6 h at 97 °C. After reaction complete, MgO was separated from the liquid and the product was subjected for HDO reaction without solvent extraction.

The condensation product identified as 4-(2-furyl)-3-buten-2-one (**2**) (λ<sub>max</sub> 316.5 nm, in MeOH) and 1,5-bis-(2-furyl)-1,4-pentadien-3-one (**3**) (λ<sub>max</sub> 367.5 nm, in MeOH) similar with Huang et al. [4]. The products easily detected by UV-Visible because the additional conjugated system promote the bathochromic shift and reduce transition energy of π→π\*. The obtained product is liquid in room temperature make it easier to handle for the following procedure.

The HDO reaction was performed using the liquid products from condensation reaction. The liquid was directly transferred to autoclave contain with activated Ni/SiO<sub>2</sub>-Cu/SiO<sub>2</sub> catalyst. The reaction conducted at 150 and 180 °C for 2 h with H<sub>2</sub> purge. The HDO products analysed by GC-MS and gave hydrocarbons (**4-5**) and oxy-compounds (**6-8**) in respective yield (Scheme 1, Fig. 4). According to Scheme 1, the hydrocarbon derivatives is octane (**4**) and trideca-1,3,5-triene (**5**), which may be obtained from HDO reaction of **2** and **3**, respectively. This is the first finding in our groups to report the production of octane using mix catalyst Ni/SiO<sub>2</sub>-Cu/SiO<sub>2</sub>. Lately, we also reported the formation of tridecane (C13) as diesel fraction using similar method but different catalyst [9]. Another product from this reaction is oxy-compounds which may produce from hydrogenation and/or deoxygenation of furfurylidene derivatives (**2-3**). It seem that compound **6-8** comes from hydrogenation of C=C alkene exocyclic followed by ring opening product.



**Scheme 1.** The predicted products from sequential condensation and HDO reaction

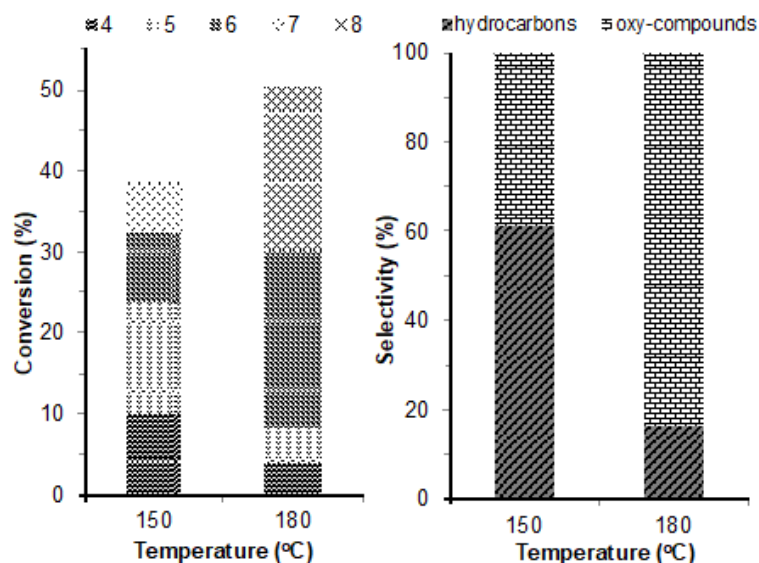


Fig 4. Conversion and selectivity of the products

The catalytic activity and selectivity of Ni/SiO<sub>2</sub>-Cu/SiO<sub>2</sub> for HDO reaction as a function of temperature are given in Fig. 4. Fig. 4 (left) showed the conversion of starting material **2** and **3** becomes hydrocarbons and oxy compounds significantly increased with increasing temperature, from 150 to 180 °C. Huang et al. reported that temperature higher than 200 °C usually needed to achieve high activity catalyst [4]. However, by using mix catalyst Ni/SiO<sub>2</sub>-Cu/SiO<sub>2</sub>, even the reaction is carried out in a lower temperature than those reported, we obtained a good performance of the catalyst (50% conversion). We considered that by using mixed catalyst, the higher dispersion of Cu in SiO<sub>2</sub> in concomitant with medium-high temperature enhance the activity for HDO reaction [7]. In Fig. 4 (right), the selectivity over hydrocarbon and oxy compound is depicted. It seems that the reaction in lower temperature gave hydrocarbon selectively than higher temperature. By this result, we consider that the mechanism reaction of HDO is very unique, especially when we used a mixed catalyst which have different activity. The mechanism is under examination and will report in next future.

## CONCLUSION

Condensation reaction of furfural and acetone gave 4-(2-furyl)-3-buten-2-one and 1,5-bis-(2-furyl)-1,4-pentadien-3-one and followed by hydrodeoxygenation using mix Ni/SiO<sub>2</sub>-Cu/SiO<sub>2</sub> gave hydrocarbon and oxy compound selectively. Reaction at 150 °C gave hydrocarbon as major products, whereas at 180 °C provided oxy-compounds as main products.

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