

Sequential Condensation and Hydrodeoxygenation Reaction of Furfural-Acetone Adduct over Mix Catalysts Ni/SiO₂ and Cu/SiO₂ in Water

Siti Mariyah Ulfa*, Rizka Fauzia Ohorella, and Caterina Widya Astutik

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Brawijaya University,
Jl. Veteran, Malang 65145, Indonesia

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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/SiO₂ and Cu/SiO₂. 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/SiO₂ and Cu/SiO₂ 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 hidrodoksigenasi dilakukan menggunakan reaktor autoklaf dengan sistem batch dalam pelarut air. Pertama, dilakukan reaksi kondensasi antara furfural dan aseton menggunakan katalis MgO diikuti dengan reaksi hidrodoksigenasi menggunakan katalis campuran Ni/SiO₂ dan Cu/SiO₂. Katalis Ni/SiO₂ dan Cu/SiO₂ 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 hidrodoksigenasi. 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: hidrodoksigenasi; 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/SiO₂ and Pd/Al₂O₃ 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 use of non-noble metal catalyst, such as Ni, Cu and Fe supported on SiO₂ was mainly reported for hydrogenolysis [4-5], pyrolysis reaction [6] and methane decomposition [7]. In my knowledge, there is a limited publication using Ni/SiO₂ or Cu/SiO₂ catalyst for HDO in liquid phase except the use of Ni-Cu/SiO₂ 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/Al₂O₃-ZrO₂ gave tridecane (C₁₃) as diesel fraction

* Corresponding author.
Email address : ulfa.ms@ub.ac.id

[9]. However, Chen et al. (2014) reported that HDO reaction of furfural derivatives using Ni-Cu/SiO₂ 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/SiO₂-Cu/SiO₂ 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(NO₃)₂•6H₂O (Merck), Cu(NO₃)₂•3H₂O (Merck), SiO₂ (Merck), Na₂SO₄ (Merck), aqua demineralized (Hydrobat), dichloromethane, n-hexane, ethyl acetate, and MgO in technical grade supplied by local vendor. Nitrogen (N₂) and hydrogen (H₂) 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/SiO₂ and Cu/SiO₂ catalysts

The catalyst Ni/SiO₂ was prepared according to Zaccheria method with modification [10]. Nickel loading is prepared for 20% by diluted 9.91 g of Ni(NO₃)₂•6H₂O salt in demineralized water then stirred until homogenous solution is formed. The solution of nickel salt then precipitated by addition of NH₄OH solution until pH 9 to form Ni(OH)₂. SiO₂ (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 N₂ gas flowing. The

catalyst was reduced at 550 °C for 2 h using H₂ gas. The Ni/SiO₂ catalyst was obtained in 8.25 g.

The catalyst Cu/SiO₂ was prepared in similar procedure with previous. The Cu(NO₃)₂•3H₂O (7.6 g) was diluted in water, added with NH₄OH until pH 9 then added with 8 g of SiO₂ 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/SiO₂ 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 N₂ 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/SiO₂ and 0.02 g Cu/SiO₂ by heating in the batch reactor for 1 h under H₂ 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 H₂ 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/SiO₂ and Cu/SiO₂

The crystal structure of Ni/SiO₂ and Cu/SiO₂ were recorded on powder X-Ray Diffraction (XRD) using Cu-K α radiation at $\lambda = 1.5406 \text{ \AA}$ scan at $2\theta = 20\text{--}80^\circ$ with scan rate $1^\circ/\text{min}$. Fig. 1 showed the XRD pattern of crystalline SiO₂ as support material compared with the catalysts Ni/SiO₂ and Cu/SiO₂ (20% metal loading). The crystalline structure of SiO₂ were detected by the

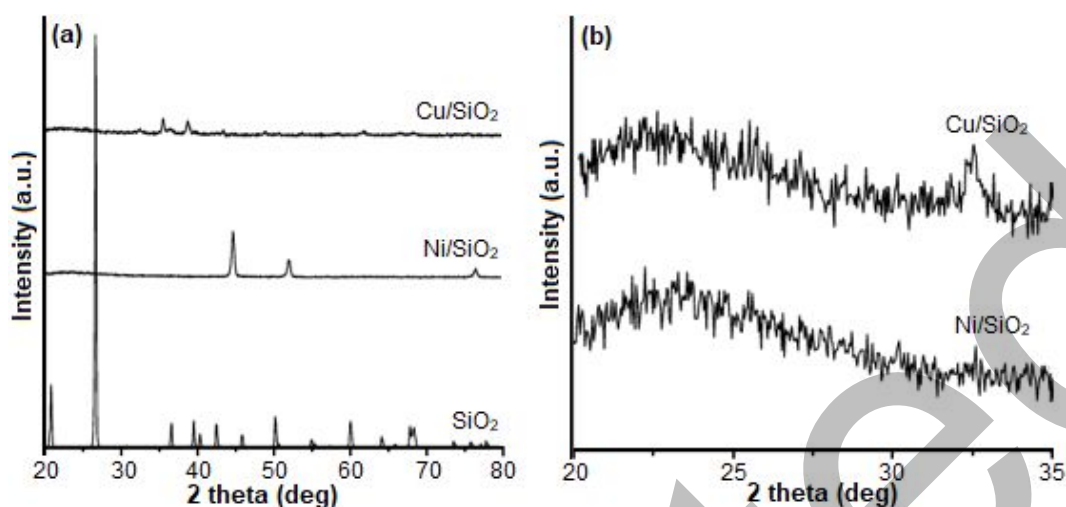


Fig 1. XRD pattern of (a) Ni/SiO₂ and Cu/SiO₂ compared with SiO₂; (b) amorphous silica profile

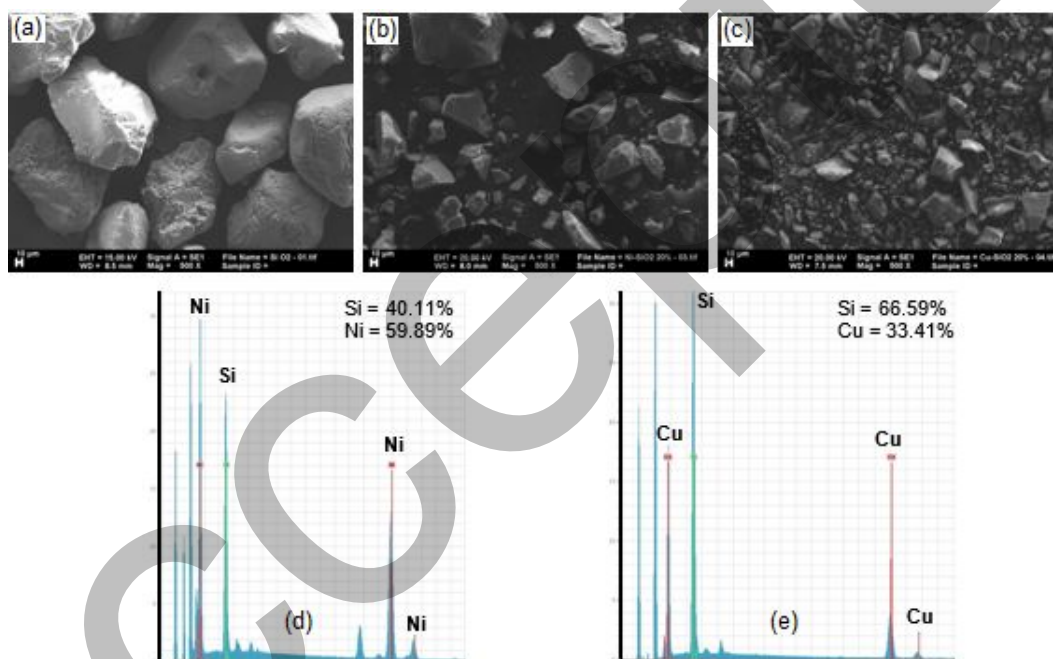


Fig 2. SEM micrographs of (a) SiO₂; (b) Ni/SiO₂; (c) Cu/SiO₂ calcined at 350 °C; (d) EDX spectra of Ni/SiO₂; (e) EDX spectra of Cu/SiO₂

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 SiO₂ by the formation of physical interaction between silica and metal [12-13]. Changing the crystallinity of SiO₂ 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/SiO₂ 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 H₂ purge completely reduced Ni²⁺ into Ni⁰ [16].

Fig. 1a (upper) present the XRD patterns of Cu/SiO₂ 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

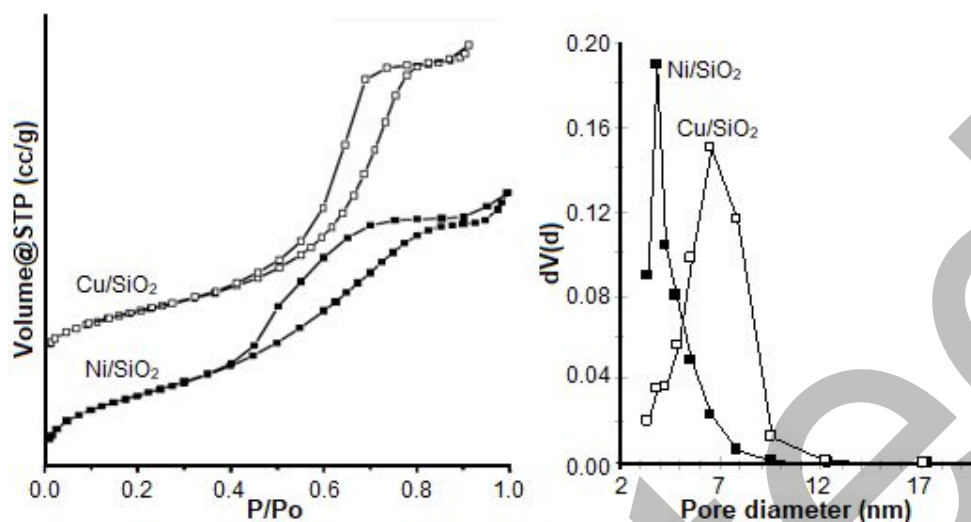


Fig 3. (a) Adsorption-desorption isotherm; (b) pore sizes distribution of catalyst

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 ₂	20	271.2	0.330	0.121	3.840	0.432
Cu/SiO ₂	20	254.4	0.553	0.112	6.601	0.432

¹ S_{BET} (surface area) BET method

² V_{meso} (volume mesoporous), D_{meso} (diameter mesoporous) BJH method

³ V_{micro} (volume microporous) SF method

⁴ 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 Cu²⁺ or Cu⁺ is reduced to Cu⁰ resulted the low intensity of Cu diffraction [18].

The surface morphology and dispersion of Ni and Cu over SiO₂ support were investigated by SEM. The representative electron micrographs of the catalysts are presented in Fig. 2. The particle size of SiO₂ (~160 μm) is larger than Ni/SiO₂ and Cu/SiO₂ (Fig. 2a). Deposition of Ni and Cu into the surface severely decreased the particle size to ~10 μm by the physical interaction between SiO₂ cage with metal. Among the three catalysts, the Cu/SiO₂ exhibit the smallest particle size compared with Ni/SiO₂ and SiO₂ (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 SiO₂ by 10³ times compared with Cu [19]. However, the low disperse metal distribution is recorded in EDX which due to sintering process [5].

N₂ adsorption-desorption isotherms of the fresh catalysts are shown in Fig. 3. It was observed that the isotherm trend of Ni/SiO₂ and Cu/SiO₂ 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/SiO₂ 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/SiO₂ 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/SiO₂ and Cu/SiO₂ displayed in Fig. 3b. In accordance with the previous analysis, Cu/SiO₂ have a large pore size ~7 nm with convergent distribution from 3~10 nm. Average pore size of Ni/SiO₂ was smaller might suggest shrinkage in pores during calcination and reduction process [12].

The BET surface area (S_{BET}) and porous structure of Ni/SiO₂ and Cu/SiO₂ is tabulated in Table 1. From Table 1, Ni/SiO₂ catalyst have a higher surface area than Cu/SiO₂ which may be caused by the optimum calcination temperature of Ni catalyst. As reported by

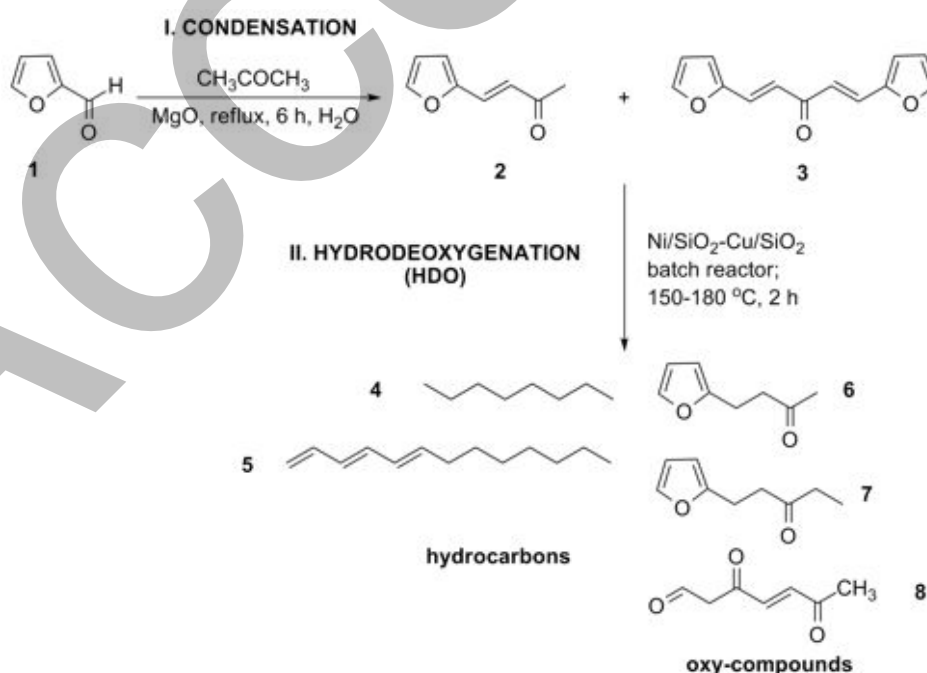
Blanco et al. (2012), calcination temperature at 500–550 °C is optimum condition for calcined and reduced Ni^{2+} become Ni^0 deposited on SiO_2 [12]. This data is supported by XRD analysis showed the sharp diffraction of Ni metal. Compared with the reported data by Ulfa et al. (2017) according to the synthesis of $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ catalysts by wet-impregnation method, the total S_{BET} of Cu/SiO_2 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_{meso}) and diameter mesoporous (D_{meso}). In overall, V_{meso} and D_{meso} of Cu/SiO_2 is larger than Ni/SiO_2 . We considered that hysteresis loop of Cu/SiO_2 which have ordered metal dispersion made the catalyst have a higher porosity than Ni/SiO_2 .

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_{max} 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 $\text{Ni}/\text{SiO}_2\text{-Cu}/\text{SiO}_2$. 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_{max} 316.5 nm, in MeOH) and 1,5-bis-(2-furyl)-1,4-pentadien-3-one (**3**) (λ_{max} 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 $\pi \rightarrow \pi^*$. 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 $\text{Ni}/\text{SiO}_2\text{-Cu}/\text{SiO}_2$ catalyst. The reaction conducted at 150 and 180 °C for 2 h with H_2 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 $\text{Ni}/\text{SiO}_2\text{-Cu}/\text{SiO}_2$. 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

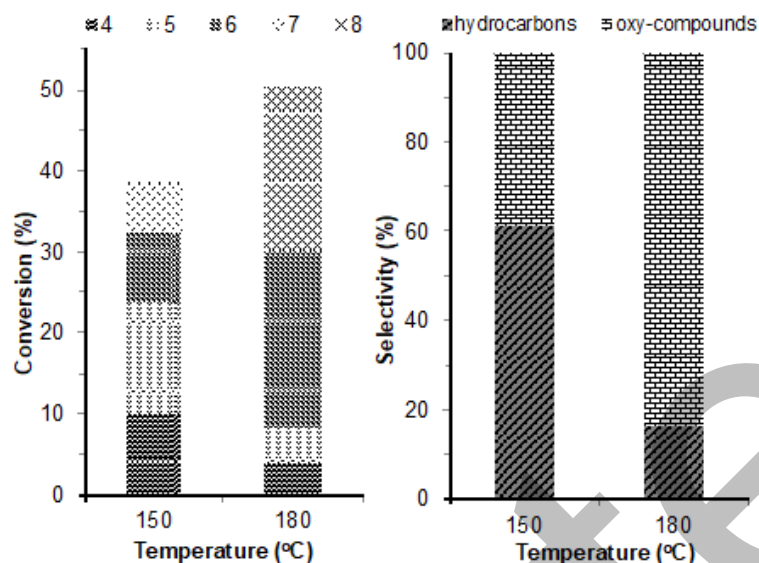


Fig 4. Conversion and selectivity of the products

The catalytic activity and selectivity of Ni/SiO₂-Cu/SiO₂ 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/SiO₂-Cu/SiO₂, 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 SiO₂ 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/SiO₂-Cu/SiO₂ 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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