

# Hydrogenation/Deoxygenation (H/D) Reaction of Furfural-Acetone Condensation Product using Ni/Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> Catalyst

Adam Mahfud, Edi Priyo Utomo, Siti Mariyah Ulfa\*

Chemistry Department, Faculty of Science, Brawijaya University, Jl. Veteran Malang 65145 Indonesia

\*Corresponding email : ulfa.ms@ub.ac.id

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## ABSTRACT

The catalytic hydrogenation/deoxygenation (H/D) reaction was carried out using Ni/Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst. The 10% (wt/wt) of Ni were impregnated on Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> (10NiAZ) by wet impregnation method followed by calcination and reduction. X-Ray diffraction analysis showed that Ni deposited on the surface, with specific surface areas (SBET) was 48.616 m<sup>2</sup>/g. Catalyst performance were evaluated for H/D reaction over furfural-acetone condensation products, mixture of 2-(4-furyl)-3-buten-2-on and 1,5-bis-(furan-2-yl)-pentan-3-one. The reaction was carried out in a batch, performed at 150°C for 8 hours. The H/D reaction gave alkane derivatives C<sub>8</sub> and C<sub>10</sub> by hydrogenation process followed by ring opening of furan in 15.2% yield. While, oxygenated product C<sub>10</sub>-C<sub>13</sub> were also detected in 17.2% yield. The increasing of the pore volume of 10NiAZ might enhance catalyst activity over H/D reaction. The alkene C=C bond was easy to hydrogenate under this condition because of the lower bond energy gap.

Key word: Hydrogenation, deoxygenation, Ni/Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>, condensation, furfural

## INTRODUCTION

Conversion of biomass into renewable fuels and chemicals become great attention among researchers, especially for the production of liquid transportation fuels [1,2]. Furfural is biobased chemicals which obtained from acid hydrolysis and dehydration of lignocellulosic material. Transformation of furfural into fuels is reported by aldol condensation with ketone followed by catalytic hydrogenation/deoxygenation (referred as H/D) to get C<sub>8</sub>-C<sub>13</sub> diesel fractions [3,4].

Condensation of furfural (**1**) with ketone have been widely reported using basic mixed oxide gave the mixture of 2-(4-furyl)-3-buten-2-on (**2**, monomer C<sub>8</sub>) and 1,5-bis-(furan-2-yl)-pentan-3-one (**3**, dimer C<sub>13</sub>) [5,6]. Ulfa et al (2015) reported the condensation of furfural and acetone by reflux produce dimer C<sub>13</sub> as major compound. However, monomer C<sub>8</sub> is observed as the main product when the reaction performed in batch reactor [7]. Since both condensation product is water-insoluble and having unsaturated double bonds of C=C and C=O, catalytic H/D reaction become fascinating to studied .

Extensive H/D reaction of lignocellulosic-based material using supported noble metal catalysts, such as Pt/SiO<sub>2</sub> [8] and Pd/C [9] have been reported. These catalysts showed excellent performance for phenolic derivatives, but the conversion or selectivity is inferior for  $\alpha,\beta$ -unsaturated aldehyde derivatives [10]. Thus, development of non-noble metal catalysts, such as Ni-based metal catalyst is worthy of H/D reaction.

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The support for the metal is another key factor determining the successful of H/D reaction. Alumina ( $\gamma\text{-Al}_2\text{O}_3$ ) was known as good support for deoxygenation of the oxygenated compound for producing hydrocarbons. It has a high surface area and Lewis acid site to activate the interaction with  $\text{H}_2$ . However,  $\gamma\text{-Al}_2\text{O}_3$  have a metastable structure which will transform into boehmite when the reaction is performed in water solvent. In addition, the formation of coke is easily deposited on its surface thus decrease the activity [11]. To overcome this problem, we promote the use double oxide support catalyst to enhance its performance. By the addition of zirconia ( $\text{ZrO}_2$ ) as second metal oxide supposed not only enhance the stability of the catalyst but also promote adsorption and dissociation of water on the surface of catalyst [12].

In this work, we report the preparation of Nickel-based catalysts supported on  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  (NiAZ) for the H/D reaction of furfural-acetone condensation products into hydrocarbon derivatives under water solvent. This reaction is interesting to study because the substrate consists with alkene C=C, furan C=C, acyl C=O and furan C-O-C in conjugated systems, then various reaction products can be expected.

## EXPERIMENT

### Chemicals and instrumentation

Furfural was obtained from Sigma-Aldrich with purity >98% and used without further purification. Ultra-High-Purity (UHP) nitrogen gas (>99.99%) and hydrogen gas from a local vendor. Nickel(II) nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), Zirconium(IV) oxide chloride octahydrate ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ), and aluminum oxide ( $\gamma\text{-Al}_2\text{O}_3$ ) were supplied by Merck Germany. Acetone, methanol, and dichloromethane are from Merck Germany. Magnesium oxide (MgO) was obtained from the local vendor and used after calcination at  $650^\circ\text{C}$  for 2 hours.

Instrumentation used for analysis are Shimadzu UV-Vis 1600Series, Shimadzu FTIR 8400S (sample analyzed using NaCl plate), GCMS QP5050A Shimadzu with FID detector and ZB-1MS column.

### Procedure reaction

#### Catalyst preparation

$\text{Ni}/\text{Al}_2\text{O}_3\text{-ZrO}_2$  (referred as Ni/AZ) were prepared with 10%wt Ni loading (10Ni/AZ) using wet impregnation refers to Zhang methods [4] with some modification.  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (9.15 g) were dissolved in distilled water with continuous stirring and ammonium solution dropped slowly into the solution until  $\text{pH} = 8$ . After  $\text{Zr}(\text{OH})_4$  precipitate appears, 3.5 g of  $\gamma\text{-Al}_2\text{O}_3$  added and stirred for 12 h at  $75^\circ\text{C}$ . Afterward, the precipitate was filtered and washed with distilled water to remove excess of chloride ions completely. Composite of  $\text{Al}_2\text{O}_3\text{-Zr}(\text{OH})_2$  were dried at  $120^\circ\text{C}$  for 24 h then calcined at  $550^\circ\text{C}$  for 5 h under  $\text{N}_2$  flowing. The obtained powder was denoted as  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  (referred as AZ). An appropriate amount of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (10%wt Ni over AZ) was dissolved in distilled water and stirred for 24 h at room temperature. After filtration, the obtained solid was dried overnight at  $120^\circ\text{C}$ , calcined at  $550^\circ\text{C}$  for 5 h and reduce at  $500^\circ\text{C}$  for 5 h using  $\text{H}_2$  flow. The obtained catalyst 10%wt  $\text{Ni}/\text{Al}_2\text{O}_3\text{-ZrO}_2$  denoted as 10NiAZ.

#### Catalyst characterization

The crystalline structure of 10NiAZ was investigated by X-ray diffraction (XRD) Pan Analytical Expert MPD measurements using Cu-K $\alpha$  radiation ( $\lambda=1.5406 \text{ \AA}$ ) at 40 kV and 30 mA. Diffraction pattern was scanned at  $2\theta = 20\text{--}80^\circ$ . Morphology and particle size of 10NiAZ were observed using Scanning Electron Microscopy (SEM) Hitachi TM3000

connected to EDX Swift ED3000 analyzer. The actual Ni loading was analyzed using XRF PANalytical Type Minipal 4. The BET surface areas, average pore diameter, and pore volume were measured by N<sub>2</sub> adsorption at -196°C using Quantachrom NOVA 1200 after degassed at 300°C.

### Activity test for Hydrogenation/Deoxygenation (H/D) reaction

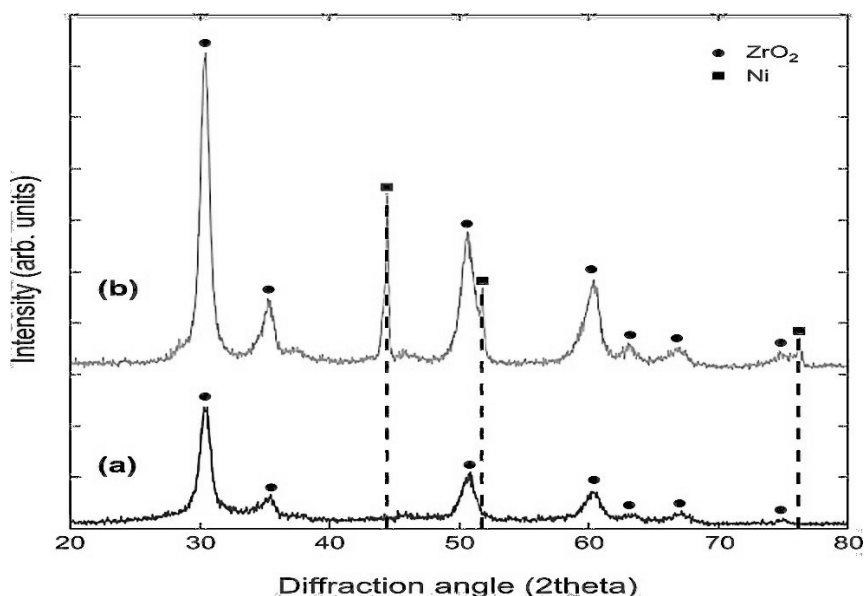
Condensation of furfural and acetone were carried out in autoclave oil batch reactor equipped with a magnetic stirrer. The reactor was loaded with 0.4 g of activated MgO, furfural (**1**) (2 mL, 0.0121 mol), acetone (3.6 mL, 0.042 mol), and 20 mL of deionized water. Air is purged out from the reactor by vacuum and flowed by nitrogen gas up to 40 psi before starting the condensation reaction. The reaction was carried out at 100°C for 6 h. The condensation product obtained as a mixture of 2-(4-furyl)-3-buten-2-one (**2**) and 1,5-bis-(furan-2-yl)-pentan-3-one (**3**) after characterized by UV-Vis spectrophotometer, FTIR, and GC-MS.

The H/D reaction was carried out in the liquid phase using batch reactor. For each reaction, activated 10NiAZ (0.02 g), the mixture of **2** and **3** (0.5 g), and solvent (CH<sub>3</sub>COOH: H<sub>2</sub>O, 19:1 v/v) were added to the reactor. After purging air, the reactor was pressurized with H<sub>2</sub> gas until 40 psi. The reactor was heated at 150°C for 8 h. The liquid reaction product was filtered and extracted using ethyl acetate, then analyzed by GC-MS.

## RESULT AND DISCUSSION

### Characterization of Catalysts

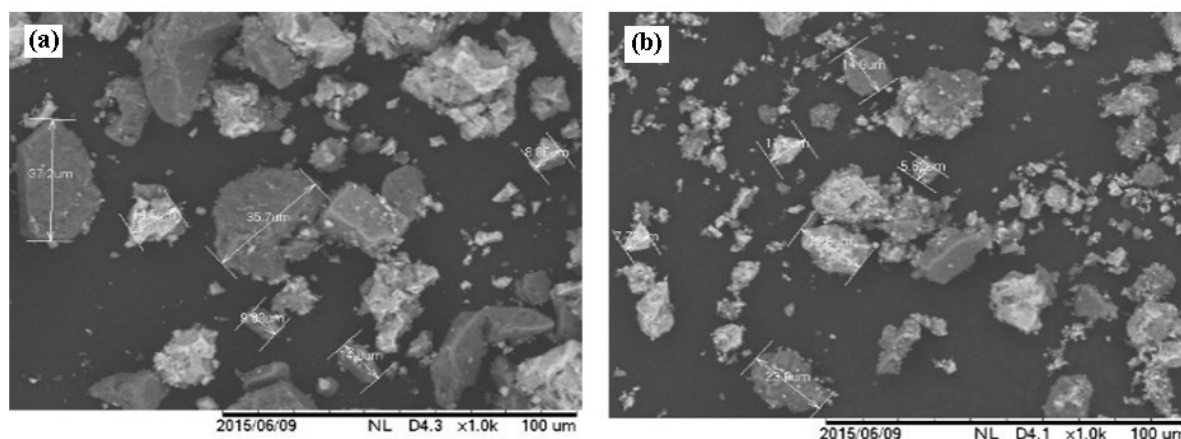
The XRD patterns of the AZ and 10NiAZ are presented in **Figure 1**. The peak was identified according to JCPDS reference standard. Compared with AZ catalyst, 10NiAZ showed the additional peak at  $2\theta = 37^\circ$ ,  $43^\circ$ , and  $64^\circ$  corresponds to metallic nickel (Ni<sup>0</sup>) in the lattice form Ni(111), Ni(200), Ni(220). An additional peak at  $2\theta = 30^\circ$ ,  $35^\circ$ ,  $50^\circ$ ,  $60^\circ$ ,  $63^\circ$



**Figure 1.** Diffractogram of (a) AZ support and (b) 10NiAZ catalyst

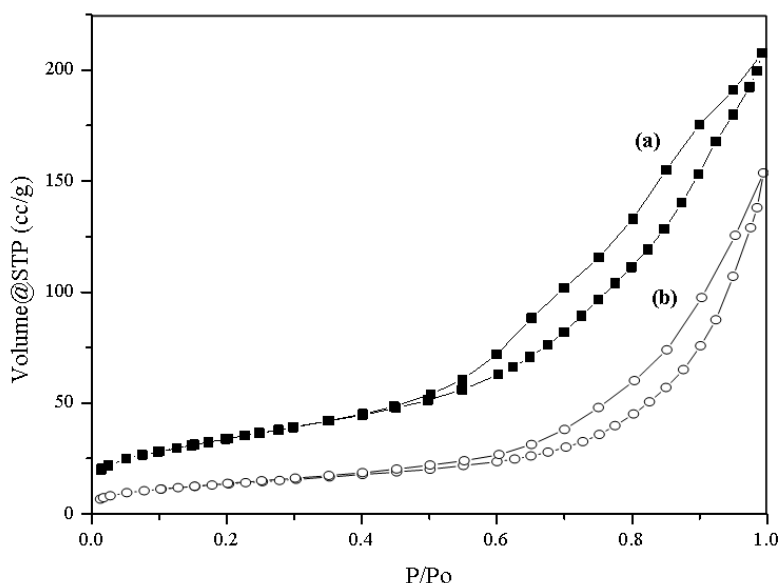
is observed as ZrO<sub>2</sub> in cubic phase [13]. Calcination of the catalyst at 500°C under hydrogen flowing successfully reduced nickel oxide (NiO), since there is an absence of diffraction at 2θ

= 37°, 43°, and 64°. However, the diffraction peak of Al<sub>2</sub>O<sub>3</sub> was not detected because the amorphous Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> composite was formed. Impregnation of Ni significantly inhibited the crystallization of individual Al<sub>2</sub>O<sub>3</sub> crystal as reported by Han et al (2013) [14].



**Figure 2.** SEM micrograph of (a) AZ support and (b) 10NiAZ catalyst (1000x optical zoom)

Profil of AZ and 10NiAZ under Scanning Electron Microscope (SEM) were displayed in **Figure 2**. After impregnation of nickel, the morphology of 10NiAZ catalyst is different compared to the support. The 10NiAZ catalyst exhibits smaller particle size with irregular shapes. The existence of nickel change the morphology of AZ and reduced the particle size [13]. The percentage of metal loading was analyzed by X-Ray Fluorescence (XRF) in **Table 1**. The Ni particles are well dispersed on the surface and the actual Ni was 10.2%, higher than the expected with relative error under 10% which is insignificant.



**Figure 3.** N<sub>2</sub> adsorption-desorption of (a) AZ support and (b) 10NiAZ catalyst

The BET surface area, pore volume and pore diameter of catalysts were measured by Quantachrome NOVA 1200 with isotherm graph depicted in **Figure 3**. All the samples showed type IV isotherms with hysteresis loops at P/Po = 0.6–1.0. It is indicating that all the catalysts are consist of mesopore with pore diameter between 5–8 nm (**Table 1**). The AZ

support has large surface areas (122.945 m<sup>2</sup>/g) and large pore volume (0.330 cc/g). For 10NiAZ catalysts, showed the decreasing surface area (48.616 m<sup>2</sup>/g), and pore volume (0.199 cc/g) by Ni deposition on AZ support, similar with the reported data by Han (2013) [15]. In contrast, the pore diameter of 10NiAZ is higher than AZ support because of the decreasing of 10NiAZ catalyst particle size. This could be proved with SEM results before and after loading (**Figure 2**). However, the characteristic of the catalyst is an important factor accounting for the activity of H/D reaction.

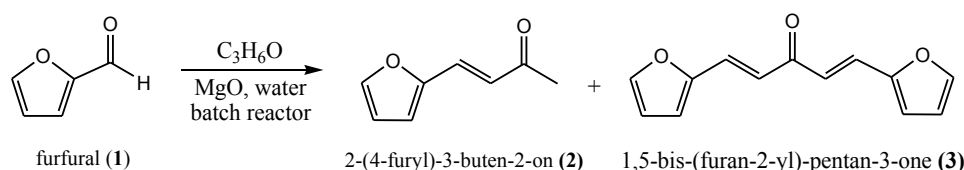
**Table 1.** Physical properties of AZ support and 10NiAZ catalyst

Catalyst	Metal Loading (%) <sup>a</sup>	S <sub>BET</sub> (m <sup>2</sup> /g)	Pore Volume (cc/g)	Pore Diameter (nm)
AZ	-	122.945	0.330	5.639
10NiAZ	10.2	48.616	0.199	7.763

<sup>a</sup>According to X-Ray Fluorescence analysis

### Activity test for Hydrogenation/Deoxygenation (H/D) reaction

The condensation reaction of furfural (**1**) and acetone was carried out in a batch reactor using MgO as a catalyst in the presence of water as a solvent. The condensation product was obtained after filtration and extraction using dichloromethane. Analysis of the products by UV-Vis spectrophotometer showed a bathochromic shift from  $\lambda_{\max}$  271 nm (furfural, **1**) to  $\lambda_{\max}$  at 318 and 383 nm, by the addition of conjugated system [7]. The condensation product showed in **Scheme 1**, that is the mixture of 2-(4-furyl)-3-buten-2-on (**2**, monomer C<sub>8</sub>) and 1,5-bis-(furan-2-yl)-pentan-3-one (**3**, dimer C<sub>13</sub>), similar with previously report [5,13]. Based on Gas Chromatography (GC-MS) analysis, conversion of **2** and **3** was 80% with selectivity over **2** achieved at 52.5%.

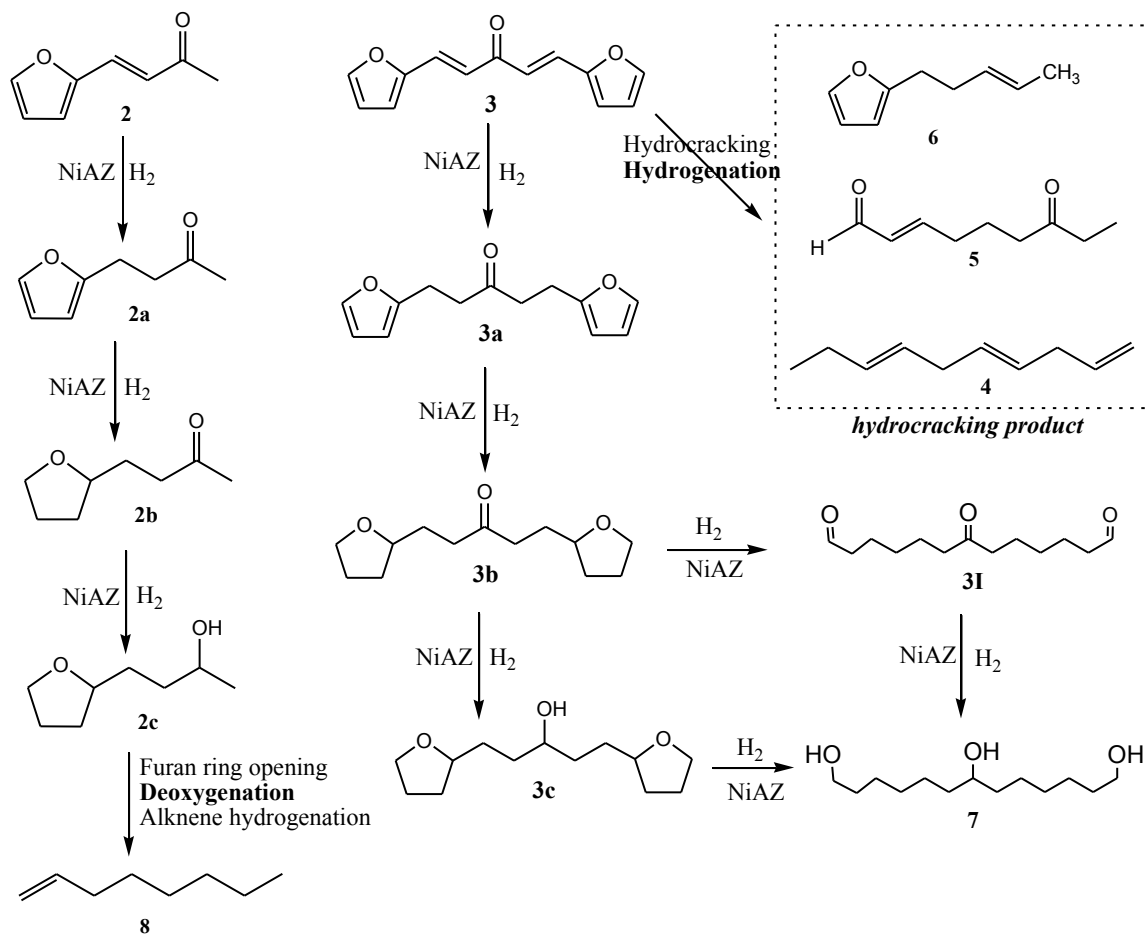


**Scheme 1.** Condensation of furfural with acetone over MgO catalyst

The mixture of **2** and **3** was directly hydrogenated/deoxygenated (H/D) using 10NiAZ as a catalyst. The reaction was carried out in a batch reactor using acetic acid and water (1:19 v/v). Prior H/D reaction, the reactor purged with H<sub>2</sub> gas until 40 psi to start the hydrogenation. After heated at 150°C for 8 h, the product was analyzed using GC-MS. The H/D product using 10NiAZ catalyst is detected as the mixture of alkane derivative and oxygenated product (**4–8**) with total carbon yield was 32.4%. Since the reaction conducted in the batch reactor, multistep or parallel reaction occurs giving a mixture product [16]. Plausible reaction pathways to access the products was depicted in **Scheme 2**, involved hydrogenation, deoxygenation, hydrocracking, and ring opening reaction. Alkane derivatives product **8** (C<sub>8</sub> alkane) was obtained from the hydrogenation of monomer **2**, followed by furan-ring-opening and deoxygenation of a hydroxyl group (**2a–2c**) to get saturated alkane. As reported by Li et al (2015), the hydrogenation of aliphatic C=C is easier than cyclic alkene, because the bond energy of the previous is lower [17]. The higher hydrocarbon alkane derivatives **4** (C<sub>10</sub> alkane) supposed produced from hydrogenation and hydrocracking of dimer **3**. However, the oxygenated hydrocarbon **5** and **6** were suggested by similar reaction

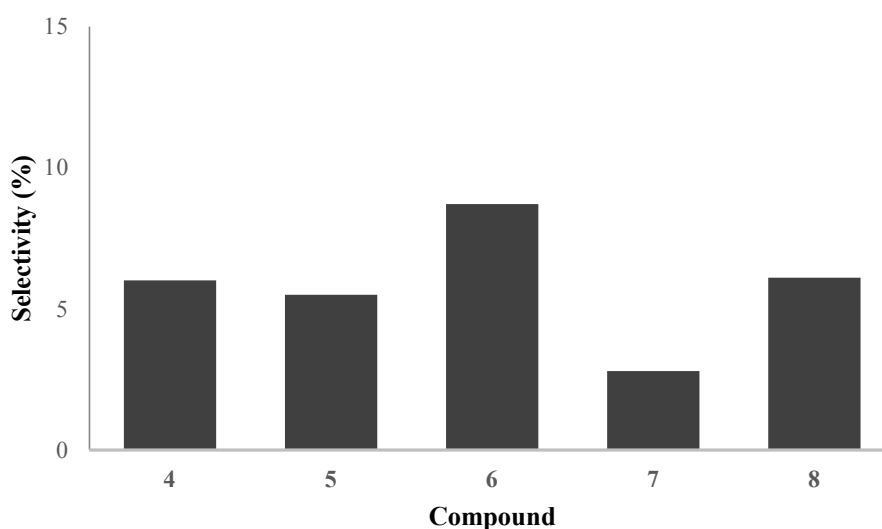


pathways, limited by partial ring opening and hydrogenation. Poly-alcohol derivatives **7** subjected from hydrogenation of dimer **3** followed by ring opening of furan (**3a-3c**) to aldehyde-ketone derivatives (**3I**). The existence of hydroxyl groups was also detected by FTIR analysis. However, these simultaneous reaction pathways with parallel reaction network were previously reported on hydrogenation/hydrodeoxygenation reaction of furfural derivatives using Raney Nickel and Pt catalysts in two-step reaction [17].



**Scheme 2.** The plausible reaction pathway to access H/D products

Product distribution from H/D reaction of the mixture of monomer **2** and dimer **3** is depicted in **Figure 4**. Total carbon yield of oxygenated products C9–C13 (**5**, **6**, and **7**; 17.2%) is still predominant among alkane derivatives C8 and C10 (**4** and **8**; 15.2%). Selectivity over oxygenated product **6** (8.7%) showed that the AZ support is relatively unstable under the hydrothermal system, compared with H/D product of the dimer using  $\text{SiO}_2\text{-ZrO}_2$  support reported by Bui et al (2011) [12]. Furthermore, the catalytic activity of 10NiAZ showed relative good performance since the aliphatic alkane **4** and **8** were selectively obtained in 6.1% and 9.1% yield, respectively. The performance of 10NiAZ can be explained by well-distribution of Ni on the support and the increasing of pore volume. These properties are activated the interaction of  $\text{H}_2$  with the metal on catalyst surface [18].



**Figure 4.** Selectivity of H/D product over 10NiAZ catalyst

## CONCLUSION

The H/D reaction of furfural-acetone condensation products using 10NiAZ was studied using batch reactor at 150°C for 8 h. The mixture of alkane derivatives C8 and C10 (15.2%) and oxygenated compounds C9–C13 (17.2%) was evaluated using GCMS. The predominant formation of oxy-compounds was explained by unstable AZ support under hydrothermal reaction. The parallel reaction initially occurs by hydrogenation reaction of C=C alkane followed by C=O and finally ring opening of C–O–C furan give alcohol derivatives.

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