

STUDY OF LIQUID ALKANES PRODUCTION FROM BIOMASS-DERIVED CARBOHYDRATES BY ALDOL-CONDENSATION AND HYDROGENATION PROCESSES

Wassana Dedsuksophon¹, Verawat Champreda² and Navadol Laosiripojana^{1*}

¹ The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Bangkok, Thailand 10140

² National Center for Genetic Engineering and Biotechnology (BIOTEC), Pathumthani, Thailand 12120

E-mail: verawat@biotec.or.th and navadol_jgsee.kmutt.ac.th*

ABSTRACT

This research aims to synthesis liquid alkanes from biomass-derived hydroxyl methyl furfural (HMF) and furfural by aldol-condensation and hydrogenation processes over several catalysts i.e. TiO_2 , $\text{TiO}_2\text{-ZrO}_2$, $\text{Pd/Al}_2\text{O}_3$ and Pd/CeO_2 . It was found that the catalysts make significant impact on the selectivity and yield of alkanes product. It is noted that $\text{Pd/Al}_2\text{O}_3$ provided the highest alkane yield and selectivity. The aldol-condensation and hydrogenation of HMF over $\text{Pd/Al}_2\text{O}_3$ provide high C12 selectivity whereas the aldol-condensation and hydrogenation of furfural over $\text{Pd/Al}_2\text{O}_3$ provide high C8 selectivity. The effects of reaction temperature, reaction pressure and reaction time were then studied. The effect of inlet furfural to acetone molar ratio was also determined. It was also found that the optimized conditions to maximize the yield of alkane production from the aldol-condensation/hydrogenation of HMF and furfural are (i) at 53°C and 24 hr for aldol-condensation of HMF, (ii) 80°C and 24 hr for aldol-condensation of furfural, and (iii) 120°C for 6 hr with HMF to acetone molar ratio of 3:1 and furfural to acetone molar ratio of 4:1 in the presence of $\text{Pd/Al}_2\text{O}_3$ (calcined at 500°C) for hydrogenation reaction.

KEYWORDS

bio-fuels, biomass, liquid alkanes, aldol-condensation, hydrogenation

I . Introduction

Currently, due to the rapid declining of petroleum resources and the rising of oil prices, it is necessary to survey for new renewable sources of energy. Furthermore, it is known that energy production from the combustion of fossil fuels usually generate CO₂, which is the main contribution of the global warming and climate change. Alternatively, fuels derived from biomass are identified as CO₂ neutral since CO₂ released during the combustion of biomass-based fuels can be later utilized for biomass growth in the next cycle [1]. Hence, nowadays, there have been several attempts globally to develop the new efficient fuels derived from biomass, which can replace the fossil fuels and minimize the environmental problem.

Typically, biomass is a renewable resource produced from organic matter including agricultural residues. For the agricultural countries like Thailand, various types and enormous amount of biomass e.g. bagasse, rice husk, rice straw, corncob, coconut, and palm are available. These materials can be effectively converted to energies in form of electricity and/or heat as well as liquid fuels via several thermo-chemical, physico-chemical, and biological processes. Theoretically, it have been reported that the products of biomass conversion can be divided into five main groups i.e. biodiesel, alcohols (ethanol/methanol), biogas, biomass-to-liquid (BTL) and hydrogen [2]. Among these biomass conversion products, BTL is one of the promising alternative fuels to replace fossil fuels in transportation section. The advantage of BTL is its identical properties to conventional liquid fuels (e.g. gasoline); hence BTL can be entirely replaced the conventional liquid fuels without any engine modification required. Furthermore, this technology can convert any type of biomass to liquid fuel with almost the same properties [3].

Liquid fuels production based on biomass consists of four steps including hydrolysis, dehydration, aldol-condensation and hydrogenation. In the first reaction step, saccharides of biomass are converted to glucose and fructose molecules by using hydrolysis process. Then, glucose and fructose molecules are converted to hydroxyl-methyl furfural (HMF) and furfural over acid catalyst by dehydration process. Finally, these intermediates are converted to liquid alkanes (C₉-C₁₅) by aldol-condensation and hydrogenation over bifunctional catalyst. This liquid alkane is an efficient renewable fuel for transportation and industrial applications. [4]. The optimum temperatures for aldol-condensation of furfural with acetone and for condensation of HMF with acetone are 80°C and 53°C respectively. The product selectivity can be controlled by the molar ratio of reactants. When the molar ratio of furfural:acetone increases from 1:9 to 1:1, the selectivity for the formation of dimer species increases by 31% and this selectivity increases further by 12% when the ratio increases from 1:1 to 2:1 [5]. The production of liquid hydrocarbon with the number of carbon atoms ranging from C₇ to C₁₅ from biomass-derived carbohydrates by acid-catalyzed dehydration, which was followed by aldol condensation over solid base catalysts to form large organic compounds. These molecules were then converted into alkanes by dehydration/hydrogenation (APD/H) over bifunctional catalysts that contained acid and metal sites [6].

In this research, we focused on the study to convert furfural and HMF to liquid alkanes via aldol-condensation and subsequent hydrogenation by varying the types of catalyst. We selected heterogeneous catalysts (i.e. TiO₂, TiO₂-ZrO₂, Pd/Al₂O₃ and Pd/CeO₂) because its easily separate and recover from the process. It is noted that TiO₂ and TiO₂-ZrO₂ promoted both hydrolysis and dehydration reactions [7]. Then, the application of TiO₂ and TiO₂-ZrO₂ for using in aldol-condensation and hydrogenation reactions was interested for this study. For Pd/Al₂O₃ and Pd/CeO₂, these catalysts lead to form C=C and C=O bonds in hydrogenation reaction over a metal catalyst [4]. The operating conditions was also studied (i.e. reaction temperature, reaction pressure, reaction time, and the catalyst/reactant molar ratio) to determine the most suitable conditions that can maximize the yield of alkane production.

II. Experimental methods

2.1 Raw material and catalyst

Furfural, HMF and acetone were purchased from Aldrich. The catalysts such as TiO₂, TiO₂-ZrO₂, Pd/Al₂O₃, and Pd/CeO₂ were used for experiments. TiO₂ was synthesized by precipitation method. For TiO₂-ZrO₂, (with Ti/Zr molar ratio of 1/1) was prepared by co-precipitation (using ZrOCl₂ and TiCl₄ as salt precursors). A solution of salt precursor was slowly dropped into a well-stirred precipitating solution of ammonium hydroxide (NH₄OH) (2.5 wt %) at room temperature. The solution was controlled at pH of 11. The

obtained precipitate was removed, and then washed with deionized water until Cl^- was not detected by a silver nitrate (AgNO_3) solution. Then, the solid sample was dried overnight at 383 K and calcined at 773 K for 6 h. For $\text{Pd}/\text{Al}_2\text{O}_3$ and Pd/CeO_2 , catalysts were synthesized using dry impregnation technique. First, Al_2O_3 and CeO_2 supports; they were commercially supplied from Aldrich. Then, $\text{Pd}(\text{NO}_3)_2$ solution (from Aldrich) (5 wt% Pd) was added with Al_2O_3 and CeO_2 supports by using dry impregnation technique. The catalysts were further calcined and reduced with 10% H_2/He at 200, 500, and 900°C for 6 h before use.

2.2 Reaction system and analysis method

The reaction was carried out in a SS 316 stainless steel small tube bomb reactor (1/2 inch O.D. and 7.5 cm. length). This reactor was mounted vertically inside a tube furnace. The temperature controller was connected to the furnace in order to heat up and control the desired temperatures. The reactor was initially loaded with the reaction mixture with catalysts and added helium up to 10 bars before starting the aldol-condensation reaction which was controlled in reaction temperature. After stopping the aldol-condensation reaction, the hydrogenation reaction was then continued by adding H_2 in the reactor and the reactor was heated to 393 K. After the controlled reaction time was reached, the reactor was quenched in a water bath to stop the reaction. This study focuses on the liquid alkanes production. The overall product yields were analyzed by gas chromatography (Shimadzu 2010 model).

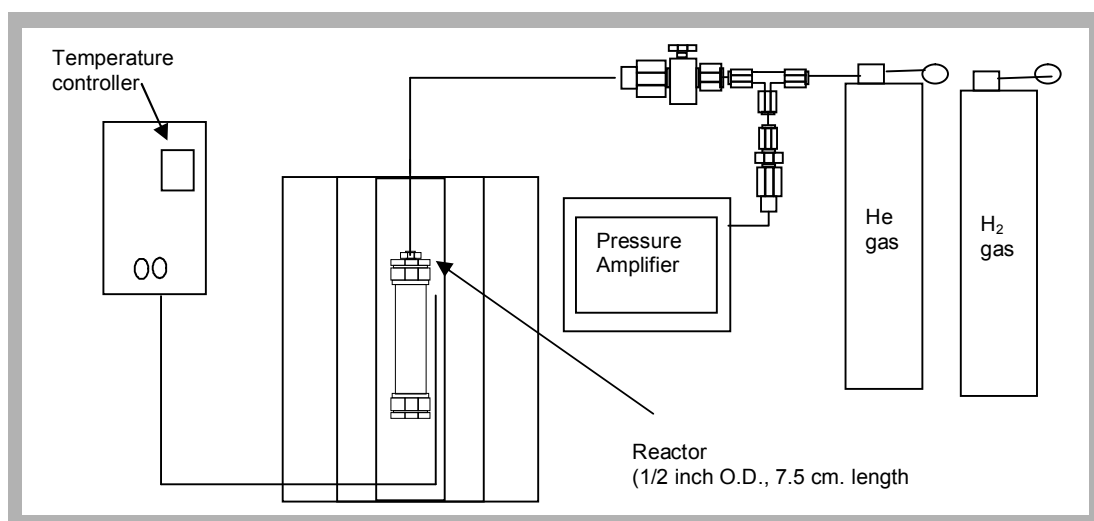


Figure 1
The experimental set up apparatus for Aldol-condensation and hydrogenation

III. Results and Discussion

There are several parameters that affect the aldol-condensation and hydrogenation processes i.e. catalysts, hydrogenation pressure and temperature, hydrogenation time, amount of catalyst and molar ratio of reactant. Hence, the effects of these parameters on the yield and selectivity of liquid alkane production were determined. It is noted that, in these experiments, HMF and Furfural were used as primary reactants.

3.1 Effect of catalyst

Firstly, the aldol-condensation and hydrogenation processes were carried out in the presence of various catalysts TiO_2 calcined at 500 °C (Ti_500), $\text{TiO}_2\text{-ZrO}_2$ calcined at 500°C and 700°C (TiZr_500, and TiZr_700), $\text{Pd}/\text{Al}_2\text{O}_3$ calcined at 200°C, 500°C and 900°C (Pd/Al_200, Pd/Al_500, and Pd/Al_900) and Pd/CeO_2 calcined at 500°C (Pd/Ce_500). It is noted that in this experiment the other parameters were controlled constantly i.e. the molar ratio of HMF to acetone and furfural to acetone at 1:1, the catalyst amount of 0.025 g, the organic to catalyst ratio of 6:1, the aldol-condensation time of 24 hr and aldol-condensation temperature of 53°C for HMF, the aldol-condensation time of 24 hr and aldol-condensation temperature of 80°C for furfural (according to the reports by Huber et al. (2005)), and the hydrogenation time of 6 hr and the hydrogenation temperature of 120°C. The hydrogenation reaction was started by adding with 25 bar 10% H_2/He in the reactor. The results of catalyst activities are shown in Figure 2 and 3. As seen in Figure 2, it can be seen that the catalysts make significant impact on the selectivity and yield of alkanes product. Clearly, among all

catalysts, Pd/Al_500 and Pd/Al_900 are the most active catalysts; the total product yield of 30.65% and 30.43% can be achieved from the aldol-condensation and hydrogenation of HMF over Pd/Al_500 and Pd/Al_900, respectively. It was also observed that the aldol-condensation and hydrogenation of HMF over Pd/Al_500 and Pd/Al_900 provide high C12 selectivity (with the C12 selectivity of 99.72% and 98.1%, respectively), whereas that of Ti_500 and TiZr_700 show lower C12 selectivity since some C8 alkane is generated.

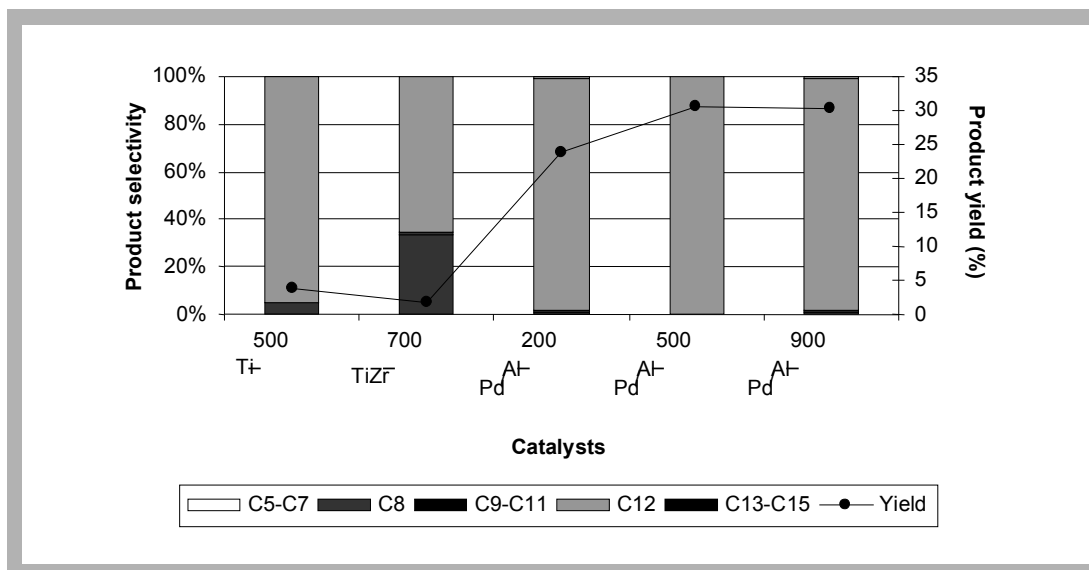


Figure 2
Selectivity and yield of alkanes from the aldol-condensation and hydrogenation of HMF over various types of catalyst

As seen in Figure 3, for the aldol-condensation and hydrogenation of furfural, Pd/Al_500 and Pd/Al_900 also provide the highest product yield of 19.28% and 19.46%, respectively. Nevertheless, the reactivities of each catalyst are closer than the reactions of HMF. Furthermore, high C8 selectivity (with the percent selectivity between 98.4-99.34%) is generated from this reaction.

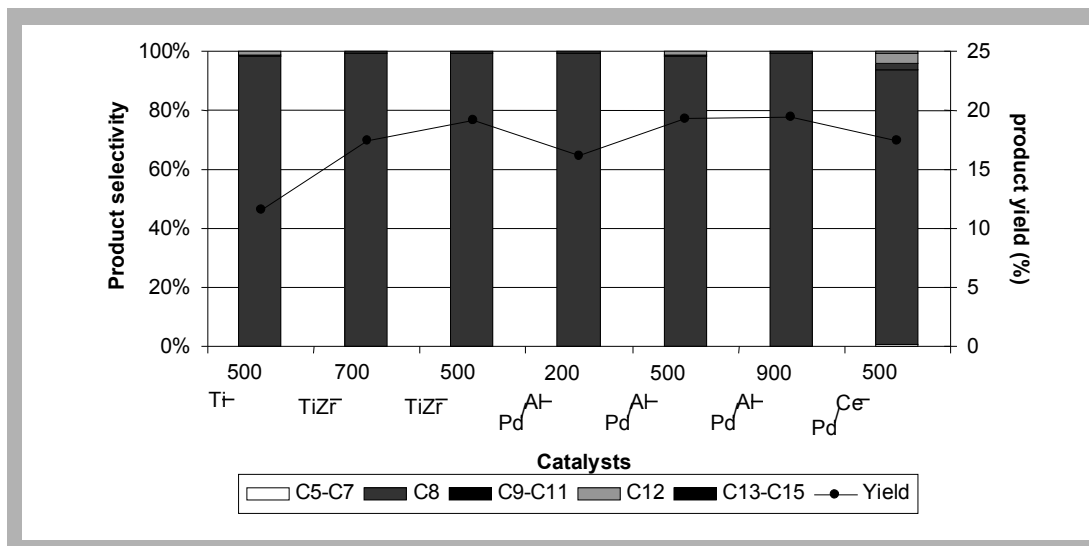
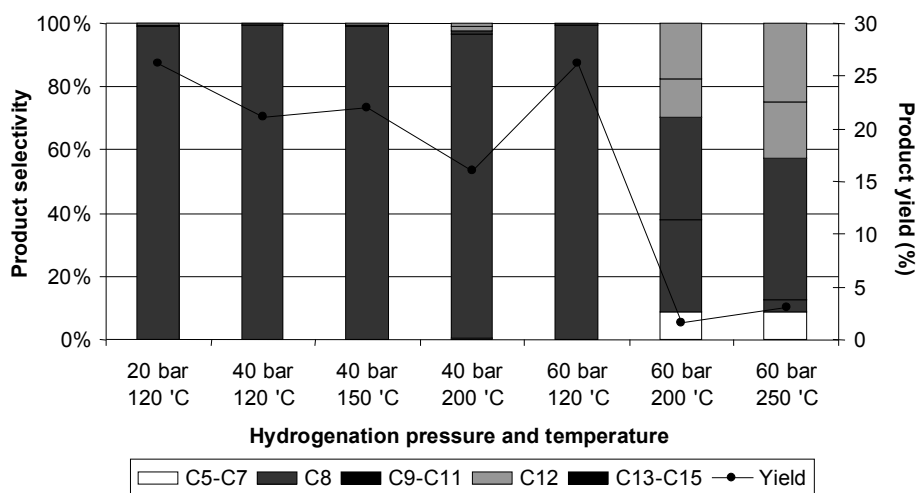


Figure 3
Selectivity and yield of alkanes from the aldol-condensation and hydrogenation of furfural over various types of catalyst

3.2 Effects of hydrogenation pressure and temperature

As the next step, the effect of reaction pressure and temperature on the product yield and selectivity from the aldol-condensation and hydrogenation of furfural was studied over Pd/Al_500. The results are shown in Figure 4; it was found that hydrogenation pressure and temperature show significant impact on both product yield and product selectivity. By increasing the hydrogenation pressure and temperature, the total product yield significantly reduced from 26.28% to less than 3% (at the reaction pressure and temperature of 60 bar, 200 °C and 60 bar, 250 °C). In addition, at higher reaction pressure and temperature, higher alkane products (C9-C11, C12 and C13-C15) were generated. We indicated from this study that the optimum pressure and temperature for hydrogenation of furfural was 60 bar, 120 °C, in which the product yield of 26.28% and C8 product selectivity of 99.48% can be achieved.

Figure 4
Selectivity and yield of alkanes at various pressures and temperatures from the hydrogenation of furfural

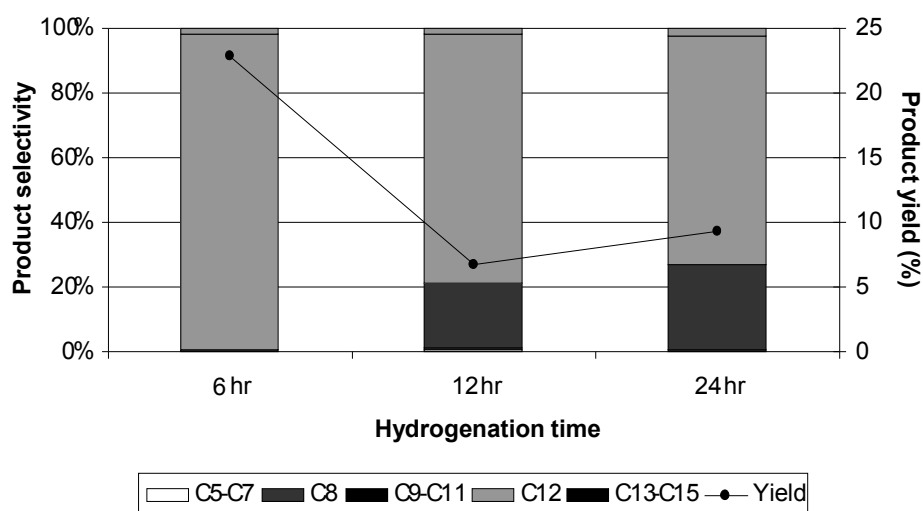


3.3 Effects of hydrogenation time

According to the results from sections 3.1 and 3.2, Pd/Al₅₀₀ catalyst with the hydrogenation pressure of 60 bar and hydrogenation temperature of 120 °C was selected for the further studies. Then, the effect of reaction time was investigated. It is noted that the other parameters were controlled constantly i.e. Pd/Al₅₀₀ of 0.025 g, organic to catalyst ratio of 6:1, the aldol-condensation time of 24 hr and the aldol-condensation temperature for the reactions of HMF and furfural at 53°C and 80°C, respectively. As shown in Figures 5 and 6, it was observed that the hydrogenation time of HMF also affects the total product yield and product selectivity.

The highest yield of liquid alkane from the aldol-condensation and hydrogenation of HMF can be achieved at the hydrogenation time of 6 hr (total yield of 22.83% can be achieved); and under this conditions, most of the alkanes generated are C12 (with the selectivity 97.68%). By increasing the reaction time to 12 and 24 hour, the total product yields considerably reduce to less than 10% and some C9-C11 alkanes are generated along with C12 alkane. According to the aldol-condensation and hydrogenation of furfural, as shown in Figure 6, the optimum hydrogenation time seems to be at 6 hr, in which the total product yield of 19.7% with the C8 selectivity closed to 100% can be gained. It is noted that, similar to the aldol-condensation and hydrogenation of HMF, the lighter alkanes (i.e. C5-C7) are generated at the longer reaction time (12 hr).

Figure 5
Selectivity and yield of alkanes at various pressures and temperatures from the hydrogenation of furfural



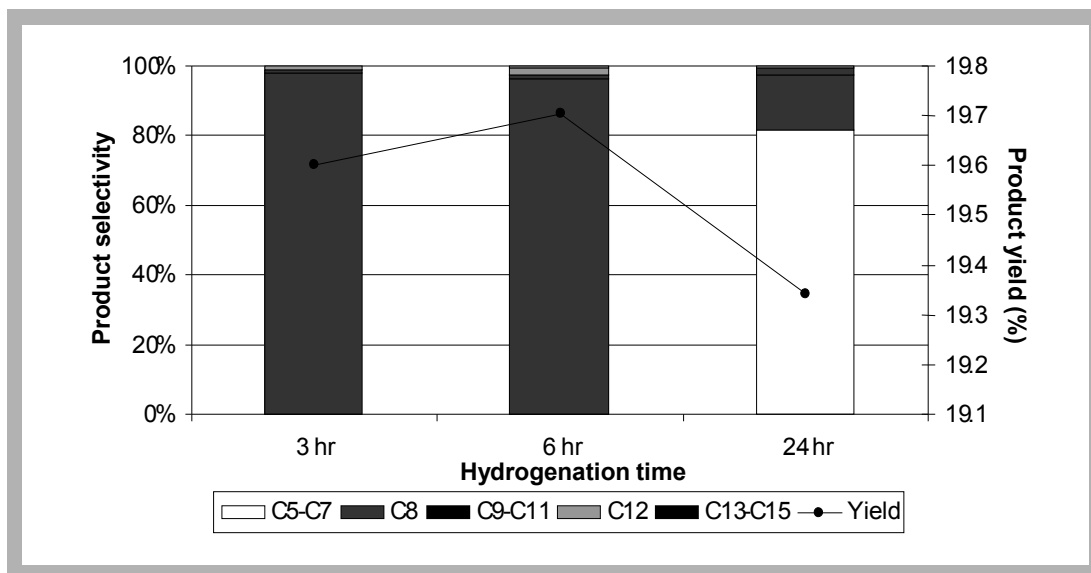


Figure 6
Selectivity and yield of alkanes from the aldol-condensation and hydrogenation of furfural at various hydrogenation times

3.4 Effects of catalyst amount

From the above studies, we found that the optimum conditions for aldol-condensation and hydrogenation of HMF and furfural are using the aldol-condensation temperature of 80 °C for 24 h following with the hydrogenation at 120°C and 60 bar for 6 hr over Pd/Al₅₀₀. The amount of Pd/Al₅₀₀ was then varied from 0.025g, 0.075g to 0.1g in order to investigate its affect on the product yield. Theoretically, higher amount of catalyst can drive the forward reaction and earn higher yield of products; as shown in Figure 7, it was observed that the increasing of catalyst helps promoting the product yield. By using Pd/Al₅₀₀ of 0.1 g, the product yield of 26.28% with C8 selectivity of 99.48% can be obtained.

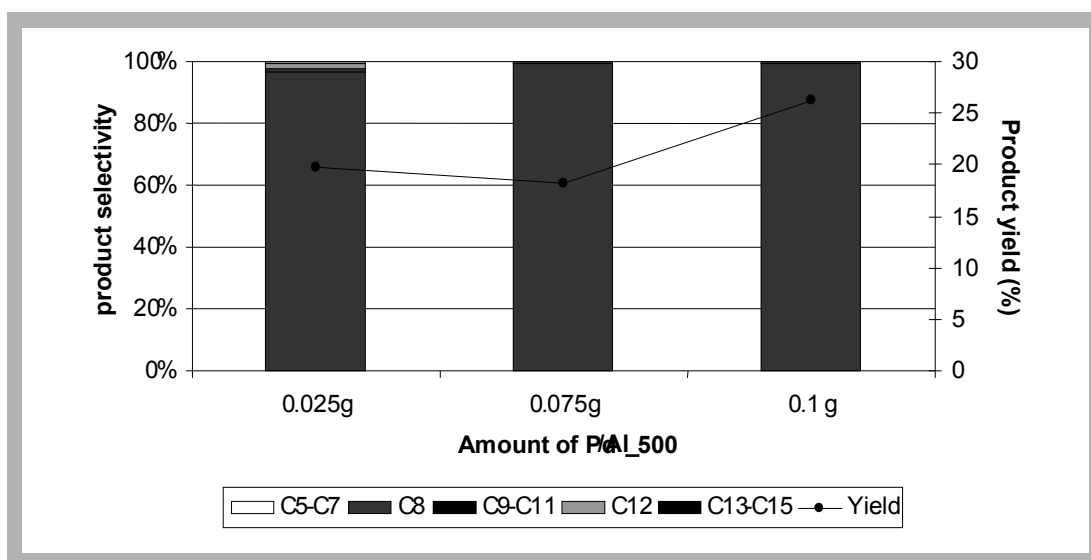


Figure 7
Selectivity and yield of alkanes from the aldol-condensation and hydrogenation of furfural at various amount of Pd/Al₅₀₀ catalyst

3.5 Molar ratio of reactant

Lastly, the effect of inlet HMF to acetone molar ratio was determined by varying the ratio of HMF to acetone from 1:1 to 2:1 and 3:1 (Figure 8); and varying the ratio of furfural to acetone from 1:1 to 2:1, 3:1, 4:1, 5:1 and 6:1 (Figure 9). It is noted that the effect of dimethylsulfoxide (DMSO) adding on the product yield and selectivity from the reactions with furfural was also studied since DMSO is important co-solvent for the hydrolysis and dehydration reactions. All reactions were carried out over Pd/Al₅₀₀ at the aldol-condensation temperature of 80°C for 24 hr following by the hydrogenation at 120°C for 6 hr.

As seen in Figures 8 and 9, the changing of inlet HMF to acetone and furfural to acetone molar ratios provide insignificant impact on the product selectivity since most of the alkanes generated are C12 and C8, respectively; nevertheless, it shows considerably positive effect on the total product yield. By increased the inlet HMF to

acetone molar ratio from 1:1 to 3:1, the total product yield greatly increased from 22.8% to 77% (Figure 8).

As for the reaction with furfural, when the inlet furfural to acetone molar ratio increased from 1:1 to 4:1, the total product yield greatly increased from 20% to 90.6%. At higher inlet furfural to acetone molar ratios (5:1 and 6:1), the positive effect became less pronounced. Furthermore, according to the reactions of with and without DMSO, it was found that DMSO adding did not restrain product yield and product selectivity (Figure 9).

From all of the above results, it can be summarized that the optimized condition of HMF and furfural conversion into liquid alkanes were using Pd/Al₂O₃ of 0.1 g, with the hydrogenation pressure of 60 bar for 6 hr and 120°C. The suitable HMF to acetone molar ratio was 3:1, while the suitable furfural to acetone molar ratio was 4:1.

Figure 8
Selectivity and yield of alkanes from the aldol-condensation and hydrogenation of HMF at various HMF:acetone molar ratios

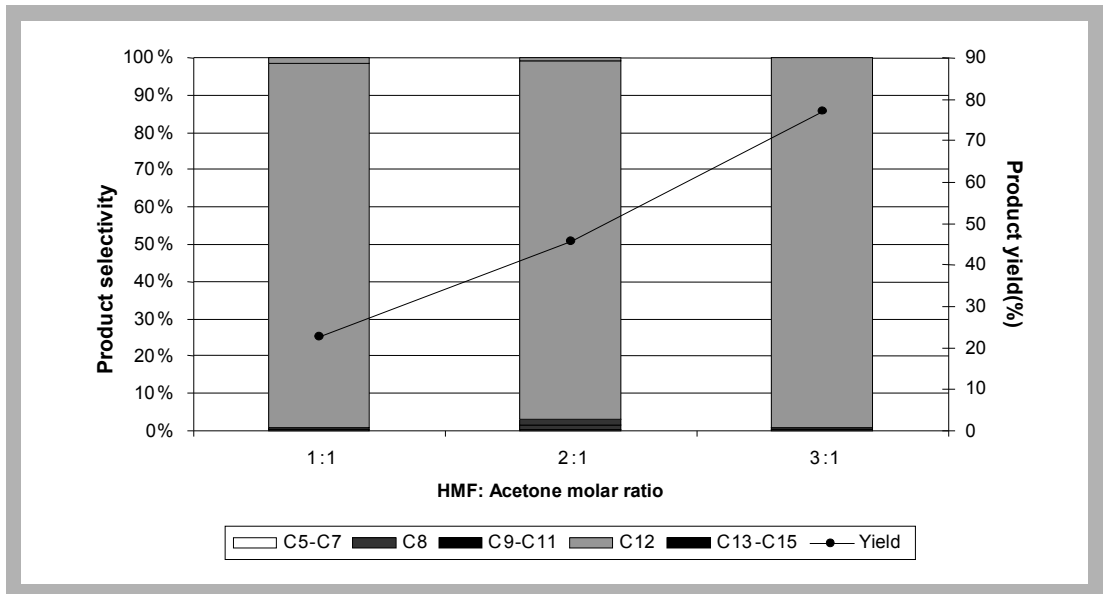
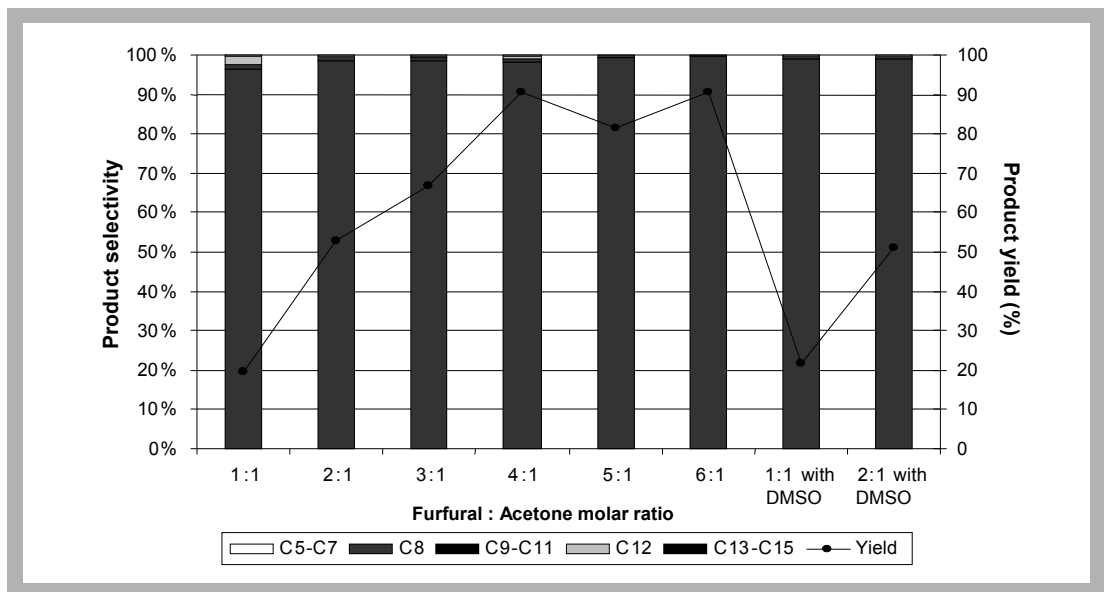


Figure 9
Selectivity and yield of alkanes from the aldol-condensation and hydrogenation of furfural at various furfural:acetone molar ratios



IV. Conclusions

This research was performed in order to study of liquid alkanes production from aldol-condensation and hydrogenation of HMF and furfural. The experiments were carried out in order to convert HMF and furfural to liquid alkane. We indicated that the optimized conditions that can maximize the yield of alkane production are (i) for aldol-condensation, the suitable temperature and time for HMF conversion are at 53°C and 24 hr, whereas those for furfural conversion are at 80°C and 24 hr; (ii) for hydrogenation, the suitable catalysts are Pd/Al₂O₃ (calcined at 500°C and 900°C) because its provided high product yield for HMF and furfural conversion to liquid alkane and the suitable operating conditions are at 120°C for 6 hr with HMF to acetone molar ratio of 3:1 and furfural to acetone molar ratio of 4:1.

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