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Development of Biofuel Production Processes from Various Feedstocks

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Abstract: Energy and environment crisis are currently among the world's most concerns. One interesting solution that several developed countries have been developing is the synthesis of clean alternative (and/or renewable) fuels to replace the conventional fossil-based fuels. On the basis of Thailand, as an agricultural country, several types and numerous amount of lignocellulosic biomass are available. Therefore, the uses of these biomasses as feedstock for biofuel (i.e. BTL and bioethanol) productions would help the nation to reduce the oil import rate as well as decrease CO_2 emission rate. In addition to biomass, palm oil is another important renewable feedstock for biodiesel production. Typically, it contains high amount of free fatty acid (FFA) that must be firstly processed or removed (as called palm fatty acid distilled or PFAD). The conversion of this PFAD to fatty acid methyl ester (FAME) is an alternative way to reduce cost and to make biodiesel enable to compete economically with conventional fuels. This article reviews our published works related to the development of processes for converting several biomasses to BTL and bioethanol and converting waste PFAD to biodiesel. In addition, along with these biofuel productions, several by-products from the processes will be further converted to energy (i.e., hydrogen) with an aim to develop the sustainable zero-waste process.

1. Introduction

Energy and environment are among the world's most concerns. Most countries around the worlds have been facing with the energy crisis due to the shortage of conventional oil as well as the dramatic rising of the oil price. These problems are believed to come from the high consumption rate of conventional oil. As a main consequence of energy crisis, several environmental problems occur. One of the current critical environmental problems is the global warming and climate change due to the high emission rate of CO_2 from the combustion of oil. Recently, there are several attempts around the world to minimize the environmental problems e.g. Kyoto protocol. According to the report of Intergovernmental Panel for Climate Change (IPCC), Thailand has signed this Protocol and has the commitment to reduce the level of green house gas releasing. Currently, although this value for Thailand is still below the world average, it has been rising up due to the growing of our fossil fuel consumption rate. Once, this value reaches or becomes higher than that of the world average, Thailand could possibly face the non-tariff trade barrier.

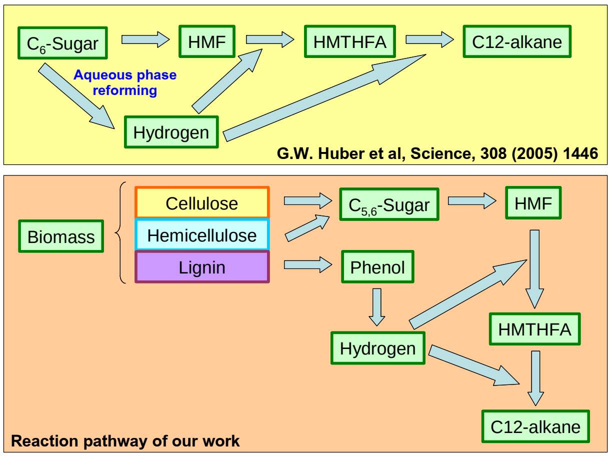
Typically, there are several procedures to minimize energy and environmental problems. One of the current interesting solution that several developed countries have been attempting to do is to develop the clean alternative (and/or renewable) fuels to replace the conventional oil. Some examples of these alternative fuels are hydrogen, gas-to-liquid (GTL), biomass-to-liquid (BTL), dimethyl-ether (DME), biodiesel, and bioethanol. Nowadays, the most practical biofuels for Thailand are bio-ethanol and biodiesel. Thai government has been attempting to promote the use of these two biofuels to replace conventional gasoline and diesel oil respectively. It should be noted that the current raw materials that have been applied to produce bioethanol and biodiesel are molasses from sugarcane, cassava, and palm oil. The major consideration for using these raw materials as feedstock for fuel production is the competition with food market, which could result in the food shortage and the rising of food price. On the basis of Thailand, as an agricultural country, we have several types and numerous amount of lignocellulosic biomass. Therefore, the uses of these biomasses as feedstock for biofuel (i.e. BTL and bioethanol) productions would be a great option for Thailand. If we can develop the efficient techniques to convert these feedstocks to biofuels, it will certainly help the nation to reduce the fuel import rate as well as decrease CO_2 emission rate from the combustion of fuel (as these alternative fuels are produced from renewable sources and the CO_2 emission from the combustion of these fuel is not considered as emission, according to Kyoto protocol). Apart from the use of biomass as raw materials for bioethanol and BTL production, palm oil is currently the main raw material for biodiesel production. Typically, palm oil always contains high amount of free fatty acid (FFA) and the presence of too high FFA easily results in high amount of soap produced during transesterification reaction. Therefore, to avoid this reaction, most of FFA in palm oil must be firstly processed or removed (as called palm fatty acid distilled or PFAD). The conversion of this PFAD to fatty acid methyl ester (FAME), which can be used as biodiesel, is an alternative way to increase the overall biodiesel yield, thus reducing the cost for biodiesel production and to make biodiesel enable to compete economically with conventional petroleum diesel fuels. Details of each study are presented below.

2. BTL production

In details, BTL is one of the promising 2nd generation fuels. Theoretically, its physical and chemical properties are identical to those of conventional diesel and/or gasoline oil (depending on the process). As for its production technology, currently, there are 2 main procedures to produce BTL i.e. Gasification/Fischer-Tropsch (FT) and fast pyrolysis processes. According to the first process, gasification/Fischer-Tropsch (FT), biomass is firstly converted to synthesis gas via gasification reaction, and then secondary reformed to liquid C_9-C_{15} alkanes via catalytic Fischer-Tropsch (FT) process. The great advantage of gasification/Fischer-Tropsch (FT) process is the achievement of high product selectivity, nevertheless, the major barrier is its poor economic feasibility. It has widely been reported that this process is economically feasible only at large scale production (3 million standard cubic meters per day; MSCMD). In contrast, for the fast pyrolysis process, it is the cheaper process and feasible for the small scale production unit, but the weakness of this process is its low product selectivity, as various types of by-products are also generated during the process. Consequently, the expensive distillation or extraction system is required.

In the year 2005, there was one article published in Science magazine (G.W. Huber et al. [1]) reporting the novel pathway for converting C_6 sugar to C_9, C_{12} and C_{15} alkanes (details are given in literature review section). Their reaction pathways involve dehydration, hydrogenation and aldol condensation reactions. We developed the process related to these reaction pathways, but instead of C_6 sugar, biomass (e.g. bagasse) was applied as our raw material. As the typical compositions of biomass are cellulose, hemicellulose and lignin, in order to convert biomass to alkane, one more reaction i.e. hydrolysis is required to convert cellulose and hemicellulose in biomass to C_6 and C_5 sugars, respectively. Figure 1 shows the comparison between G.W. Huber et al. and our reaction pathway.

In our study, the integrative hydrolysis/dehydration/ aldol-condensation/ hydrogenation of lignocellulosic-biomass (corncob) and biomass-derived carbohydrate (tapioca flour) in the single reactor for producing water-soluble C_5-C_{15} organic compounds, which can be later converted to alkane-based fuel, was developed. It was found that WO_3-ZrO_2 efficiently catalyzes the hydrolysis/dehydration of these feedstocks to 5-hydroxymethylfurfural and furfural, while the impregnation of Pd over WO_3-ZrO_2 was active for the sequential aldol-condensation/hydrogenation of these furans to C_5-C_{15} compounds. The single use of Pd/WO_3-ZrO_2 for these integrative reactions was studied and the optimum conditions for maximizing C_5-C_{15} yield were observed at the hydrolysis/dehydration temperature of 300°C for 5 min; aldol-condensation temperature of 80°C for 30 h; and hydrogenation temperature of 120°C for 6 h. It was revealed that C_5-C_{15} yield from tapioca flour is higher than corncob; furthermore, the reaction of tapioca flour produced higher C_6/C_9/C_{15} compounds, whereas corncob generated more C_5/C_8/C_{13} compounds (Figure 2). These differences are related to the containing of lignin and hemicellulose in corncob. The novelty of our previous work is that we combined all reactions (i.e. hydrolysis, dehydration, hydrogenation and aldol condensation reactions) in a single reactor unit. The great benefit for the use of single reactor unit is its user-friendly and easy operation. As the major difficulty for biomass utilization is its low density and high distribution, consequently the cost for biomass transportation is high and thus it may not be suitable for large-scale plant. The decentralized biomass conversion would be a good option to overcome the above problem, and the user-friendly system with simple operation is required.



G.W. Huber et al, Science, 308 (2005) 1446

Reaction pathway of our work

Figure 1. Comparison of reaction pathway in G.W. Huber et al. and our work.

3. Lignocellulosic ethanol production

According to the research on lignocellulosic ethanol production, there are 2 main reactions involved i.e. hydrolysis of biomass to C_5 and C_6 sugars and fermentation of these sugars to ethanol. For the hydrolysis reaction, currently, the technology is based on the acid hydrolysis (using sulfuric acid). Nevertheless, environmental concern is the barrier of this process. The use of enzymatic technology can solve the above problem but the high cost of enzymes and the requirement for prior physical or chemical pretreatment of biomass limits the use of this process in commercial scale. As another novel process, hot compressed water (HCW) technology has been proposed to have good capability to hydrolyze cellulose and hemicellulose in biomass to C_6 and C_5 sugars, respectively. It should be noted that the key barrier of HCW technology is the occurring of side reaction i.e. dehydration simultaneously with hydrolysis reaction, which further converts sugar to furfural components (e.g. furfural and hydroxyl-methyl-furfural; HMF). According to our study, we found that in the presence of suitable catalyst (i.e., solid super-acid catalyst) under HCW condition, our catalyst can promote the hydrolysis reaction simultaneously with inhibit the dehydration reaction. The successful development of this catalyst and reaction condition will help promote the use of this technology for lignocellulosic ethanol production. As for the fermentation part, ethanol fermentation is a biological process in which organic materials, mainly sugars, are converted by microorganisms to ethanol. The most commonly used microbe is *Saccharomyces cereviciae*, which is the preferred one for most ethanol fermentation, while research and develoment on alternative ethanologenic microorganisms has been an important issue. *Candida tropicalis* has been a promising candidate for ethanol fermentation from lignocellulosic biomass as it can use xylose for fermentation and tolerates to polyphenolic compounds in biomass hydrolyzate.

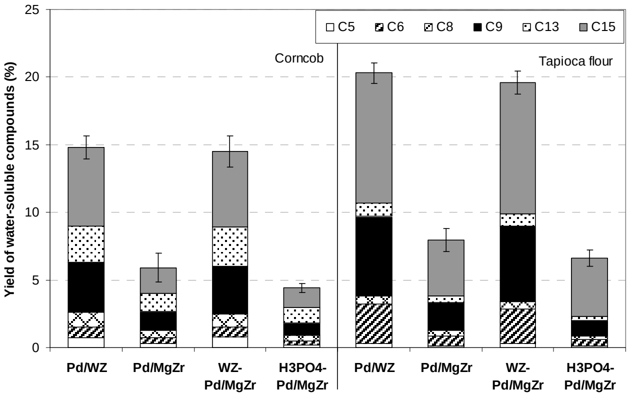


Figure 2. Yield of water-soluble C_5-C_{15} organic compounds from the integrative hydrolysis/dehydration/aldol-condensation/hydrogenation of corncob and tapioca flour in the presence of various catalyst systems [2].

4. Biodiesel production

Regarding biodiesel production process, currently, palm oil is the main raw material since it constitutes a renewable and sustainable source of energy. Importantly, palm oil always contains high amount of free fatty acid (FFA) and the presence of too high FFA easily results in high amounts of soap produced simultaneously with the transesterification reaction. To avoid this reaction, most of FFA in palm oil must be firstly processed or removed (as called palm fatty acid distilled or PFAD). Recently, several works in the literature have reported the possible conversion of this PFAD to fatty acid methyl ester (FAME) via esterification as a good procedure to reduce the cost for biodiesel production and consequently to make biodiesel enable to compete economically with conventional petroleum diesel fuels. The typical catalyst for this reaction is sulfuric acid, nevertheless, the main problem of using this liquid acid catalyst is the requirements of separation process as well as the good waste management system. Recently, some literatures have proposed the use of solid super acid catalyst e.g. sulfate zirconia (SO_4-ZrO_2) for this reaction. The great benefit of the solid catalyst is the easy separation from the product solution, but the current problem of typical solid catalyst is its relatively low

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reactivity compared to liquid sulfuric acid and also its easily loss of reactivity for long-term operation. Therefore, the development of soild super acid catalyst that provides high reactivity with long term stability is an important step to improve the reaction performance.

In our study, the esterification of PFADin the presence of three modified zirconia-based catalysts i.e. SO_4-ZrO_2, WO_3-ZrO_2 and TiO_2-ZrO_2 (with several sulfur- and tungsten-loading contents, Ti/Zr molar ratios, and calcination temperatures) was studied. It was found that, among all synthesized catalysts, the reaction in the presence of SO_4-ZrO_2 and WO_3-ZrO_2 (with 1.8%SO_4 calcined at 500°C and/or 20%WO_3 calcined at 800°C) enhances relatively high fatty acid methyl ester (FAME) yield (84.9-93.7%), which was proven to relate with the high acid site density and specific surface area as well as the formation of tetragonal phase over these catalysts. The greater benefit of WO_3-ZrO_2 over SO_4-ZrO_2 was its high stability after several reaction cycles, whereas significant deactivation was detected over SO_4-ZrO_2 due to the leaching of sulfur from catalyst (Figure 3). For further improvement, the addition of toluene as co-solvent was found to increase the FAME yield along with reduce the requirement of methanol to PFAD molar ratio (while maintains the FAME yield above 90%). Furthermore, it was observed that the presence of water in the feed considerably lower the FAME yield due to the catalyst surface interfering by water and the further hydrolysis of FAME back to fatty acids. We proposed here that the negative effect can be considerably minimized by adding molecular sieve to remove water from the feed and/or during the reaction.

5. By-product utilization

The development of technologies for converting several by-products from above processes to energy and/or valuable products are proposed by converting these by-products to hydrogen-rich gas. Hydrogen is the major fuel for fuel cell; it can be produced efficiently from catalytic steam reforming of several conventional hydrocarbon fuels such as methane, natural gas, liquefied petroleum gas (LPG), gasoline and other oil derivatives. Nevertheless, due to the current oil crisis and the shortage of fossil fuels, the development of the hydrogen production process from biomass-based fuels and/or from wastes attracts much attention. According to our studies, we successfully converted by-products from the above reactions i.e. waste PFAD left from the reaction to hydrogen for later utilization in fuel cell (Table 1). In detail, the steam reformings of PFAD over Rh on MgO-Al_2O_3, Al_2O_3, and Ce-ZrO_2 (with Ce/Zr ratios of 3/1, 1/1, and 1/3) supports were studied. At 1023 K, the conversions of PFAD are almost 100%, while H_2, CO, CO_2, and CH_4 are the major products from the reaction with some amount of high hydrocarbon compounds i.e. C_2H_4, C_2H_6, and C_3H_6 also detectable. Among all catalysts, the highest H_2 yield with the greatest resistance toward carbon deposition and lowest formation of hydrocarbons in the product were achieved from Rh/MgO-Al_2O_3. The activities of all catalysts increased with increasing temperature; interestingly at high temperature, H_2 yields from the steam reforming over Rh/Ce-ZrO_2 (with Ce/Zr ratio of 3/1) become greater than those observed over Rh/Al_2O_3

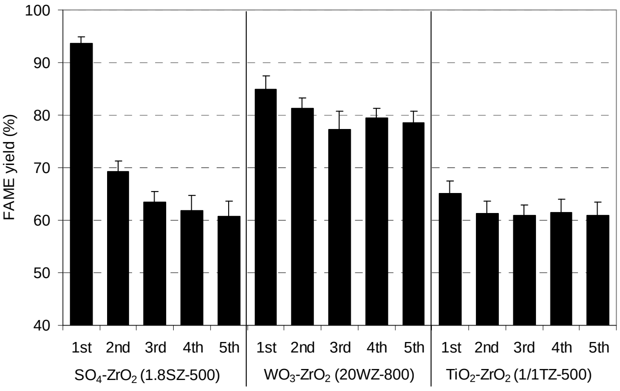

Figure 3. Reusability testing (in 5 reaction cycles) of 1.8SZ-500 (1 wt%), 20WZ-800 (0.5 wt%) and 1/1TZ-500 (1 wt%) toward the esterification of PFAD at 80°C with the reaction time of 120 min and methanol to PFAD molar ratios of 6:1 [3].

Table 1. Product distributions and degree of carbon formation after exposure in steam reforming of PFAD at 1023 K for 48 h over various catalysts [4].

Catalyst	H_2O/carbon molar ratio	Product distribution (%)							Carbon formation (mmol g_{cat}^{-1})
		YH_2	SCO_2	SCO	SCH_4	SC_2H_4	SC_2H_6	SC_3H_6	
Rh/Ce-ZrO_2 (Ce/Zr=3/1)	3.0	56.7	40.8	19.6	26.3	8.9	2.4	2.0	10.0
	5.0	58.4	43.6	17.9	28.4	7.3	1.6	1.2	9.4
	7.0	6.03	45.9	16.9	29.9	5.4	1.2	0.7	9.1
	9.0	61.2	46.9	15.9	30.9	5.1	0.9	0.3	8.6
	11.0	63.4	47.5	15.3	32.1	4.2	0.8	0.1	8.2
Rh/Ce-ZrO_2 (Ce/Zr=1/1)	3.0	60.1	40.0	21.5	24.9	9.0	4.1	0.5	10.2
	5.0	61.2	41.7	19.7	27.3	8.1	2.8	0.4	10.1
	7.0	64.5	45.5	16.5	28.2	7.5	2.1	0.2	9.7
	9.0	66.7	48.5	14.2	30.1	5.6	1.5	0.1	9.3
	11.0	68.7	50.2	13.1	31.5	4.2	1.0	0	9.0
Rh/Ce-ZrO_2 (Ce/Zr=1/3)	3.0	63.5	43.2	23.8	18.4	9.9	3.3	1.5	9.5
	5.0	65.7	45.3	22.9	19.4	8.4	3.1	0.9	9.1
	7.0	66.9	48.9	18.9	22.4	6.3	2.9	0.6	8.4
	9.0	68.4	51.2	16.1	23.6	6.1	2.5	0.5	8.0
	11.0	69.2	53.4	15.5	24.7	5.2	1.1	0.1	8.0
Rh/Al_2O_3	3.0	60.7	38.5	30.1	18.8	7.6	2.9	2.2	10.4
	5.0	63.4	40.5	29.4	20.4	5.3	2.4	2.0	9.8
	7.0	65.8	42.3	26.1	23.9	4.1	2.1	1.5	9.8
	9.0	67.2	46.5	22.2	24.9	3.2	1.9	1.3	9.6
	11.0	69.9	47.8	20.1	27.2	2.6	1.3	1.0	8.6
Rh/MgO-Al_2O_3	3.0	72.6	45.1	31.4	12.2	6.4	3.4	1.5	7.1
	5.0	74.9	47.8	29.3	13.9	5.4	2.5	1.1	6.8
	7.0	75.4	52.3	26.8	14.8	3.2	2.0	0.9	6.4
	9.0	75.9	57.9	21.9	15.7	2.2	1.8	0.5	6.3
	11.0	76.3	60.4	20.3	15.9	2.1	1.0	0.3	6.1

and Rh/MgO-Al_2O_3. This great improvement is due to gas-solid reactions between hydrocarbons present in the system with lattice oxygen (O_O^x) at Ce-ZrO_2 surfaces simultaneously with the reaction taking place on the active sites of Rh. Rh/Ce-ZrO_2 with Ce/Zr ratios of 3/1 was then selected for further study by adding O_2 and H_2 along with PFAD and steam at the feed. An addition of both components significantly reduced the degree of carbon deposition and promoted the conversion of hydrocarbons to CO and H_2. Nevertheless, the presence of too much O_2 could oxidize Rh particles and combust H_2 to H_2O, which results in low reforming reactivity. Addition of too much H_2 also reduced the catalyst activity due to the active site competition with Rh particles and the inhibition of gas-solid redox reactions between the gaseous hydrocarbon components with lattice oxygen (O_O^x) on the surface of Ce-ZrO_2 support. This by-product utilization will provide the great benefit in terms of energy, environmental, and economical aspects to the overall production unit.

6. Conclusion

In summary, this research developed the processes for converting several biomasses to biofuels (i.e. BTL and bioethanol; as called cellulosic ethanol) and also converting waste PFAD to biodiesel (as called fatty acid methyl-ester; FAME). It should be noted that, along with these biofuel productions, several by-products e.g. glycerol, lignin, and undefined residues are also generated from the reactions. As another research theme, we plan to study the processes for utilizing or converting these by-products to energy and/or valuable products with an aim to develop the sustainable zero-waste process. On this basis, it will provide the great benefit in terms of energy, environmental, and economical aspects.

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