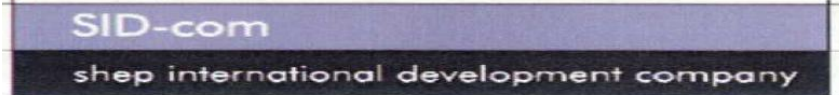


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THE PRODUCTION OF SYNTHETIC DIESEL FROM BIOMASS

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ABSTRACT

This paper discusses the potential of biomass utilization available in Thailand and alternative methods of production of synthetic liquid transportation fuel from biomass. This is to replace the conventional biofuel produced by tranesterification and fermentation processes which has some disadvantages. For example, they cannot be used directly in the automobiles without blending with conventional fossil fuels.

The integration of biomass gasification and the Fischer-Tropsch synthesis (BG-FT) and the catalytic depolymerization processes (CDP) will be considered as alternative ways to overcome the disadvantages of conventional bio-fuel. From the literature review and theoretical results of this work, CDP is the most suitable method to produce synthetic liquid transportation fuel from biomass because it can produce a higher amount of synthetic fuel than the BG-FT process. In addition, the cost of CDP is also less than the BG-FT process which consists of a two step conversion process: biomass gasification and FT-Synthesis.

KEYWORDS: synthetic diesel, biomass gasification, Fischer-Tropsch synthesis, catalytic depolymerisation process

1. INTRODUCTION

At present, the industrial and transportation sector in Thailand is developing rapidly and growing continuously. Therefore the energy demand from this sector is increasing. However, Thailand has insufficient fossil fuel resources to cover its own needs. Consequently, Thailand depends on imported crude oil from Middle Eastern countries. Today, because of the high price of crude oil, Thailand could face a potential oil crisis in the future. Therefore the government as well as private organizations are trying to find the alternative ways to resolve this issue. The use of biomass is one alternative solution, because biomass is still the cheapest fuel available in Thailand and it will be the major alternative fuel source available in the future [1-3]. In addition to solving the problem of a possible oil crisis, the utilization of biomass is CO₂-neutral, which means biomass fuel emission has no effect on the CO₂-cycle because only assimilated CO₂ is emitted. This is important because CO₂ is the primary factor in the global warming process.

Biomass could be defined as organic materials from various natural source of energy, e.g. agricultural crops and residues, wood and its residues and industrial wastes as follow [3]:

- Agricultural crop such as sugarcane, cassava, corn, etc. those are sources of carbohydrates, starch and sugar including oil containing plants.
- Agricultural residues such as rice straw from rice fields, cassava rhizome from tapioca fields, corncobs from cornfields, etc.

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- Wood and wood residues such as fast-growing trees, wood wastes from wood mills, waste from pulp and paper mills, etc.
- Waste streams such as rice husk from rice mills, bagasse from sugar refineries, residue from palm oil extraction plants, municipal solid waste, etc.

In this study, biomass can be divided into two categories: the agricultural based biomass and the wood based biomass.

Agricultural based biomass

As an agricultural country, Thailand can produce a diversity of agricultural products and their residues, respectively. The four main agricultural products of Thailand are sugarcane, rice, cassava and palm oil. Annual production of these products from crop year 00/01 to 05/06 has been reported by The Office of Agricultural Economics of Thailand [4] and is illustrated in Figure 1 below.

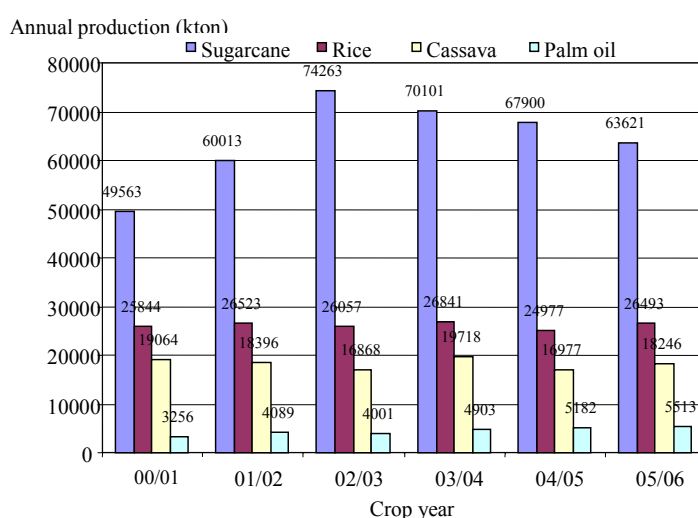


Figure 1 Annual production of agricultural products

Biomass residues of these products are bagasse and trash from sugarcane, rice straw and rice husk from rice, cassava rhizome and stalk from cassava and fiber, empty fruit bunch and shell from palm oil. The potential of these residues can be estimated from Crop-to-Residue Ratio (CRR), Surplus Availability Factor (SAF) and Lower Heating Value (LHV) of each biomass which is shown in Table 1 [3, 5-6].

The biomass potential for four main agricultural products based on crop year 05/06 is shown in Table 1 and accounts for 41.22 million tons with a total energy potential of $512.32 \cdot 10^6$ GJ. In addition to these biomass residues from the four main agricultural products, there is also biomass residue from other sources e.g. corncob, coconut, etc.

Table 1 CRR, SAF, LHV and biomass potential of four main agricultural products in 05/06

Source	Residues	CRR	SAF	LHV (kJ/kg)	Potential (kton/year)	Potential (10^6 GJ/yaer)
Sugarcane	Bagasse	0.29	0.01	7,368	184.5	1.36
	Trash	0.30	0.98	15,479	18,704.57	289.53
Rice	Rice husk	0.23	0.45	14,204	2,742.03	38.95
	Rice straw	0.45	0.78	12,330	9,299.04	114.66
Cassava	Cassava rhizome	0.46	0.98	5,494	8,225.30	45.19
	Stalk	0.09	0.70	13,380	1,149.50	15.38
	Fiber	0.15	0.13	11,800	107.50	1.27
Palm oil	EFB	0.25	0.58	7,240	799.39	5.79
	Shell	0.05	0.04	16,900	11.03	0.19

Wood based biomass

There are a large number forested areas and wood products in Thailand. However, referring to the study from [3], only three types of wood have been considered as fuel wood. These are rubber wood, eucalyptus and the palm oil tree. The annual production of rubber, palm oil and eucalyptus is shown in Figure 2 [3, 7-8].

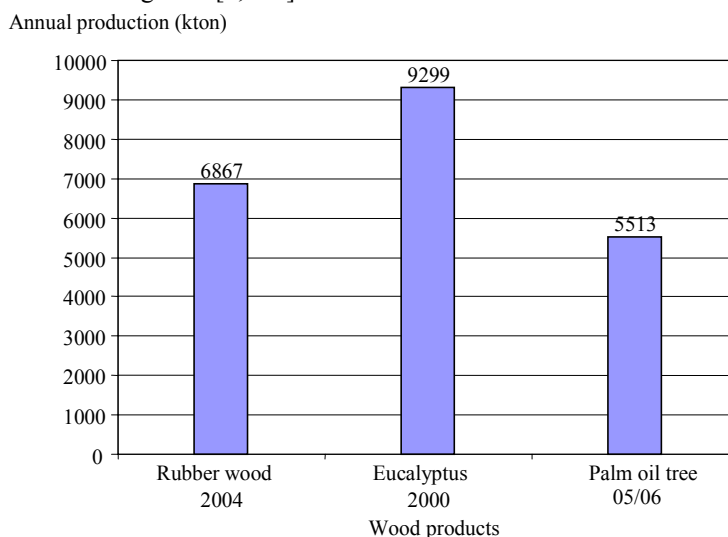


Figure 2 Annual production of woody products

The woody biomass residues can be separated into barks from forests and saw mill from wood processing. The potential of woody biomass can also be calculated from CRR, SAF and LHV, the same as for agricultural based biomass. Table 2 shows the CRR, SAF, LHV [3, 7, 9] and the woody biomass potential in Thailand.

The potential of woody biomass in Thailand amounts to 23.13 millions tons per year with an energy potential of $195 \cdot 10^6$ GJ/year.

Table 2 CRR, SAF, LHV and biomass potential of woody biomass

Source	Residues	CRR	SAF	LHV (kJ/kg)	Potential (kton/year)	Potential (10^6 GJ/yaer)
Rubber wood	Saw mill	0.20	1	13,962	1,373.44	19.18
	Bark	0.40	1		2,746.89	38.35
Eucalyptus	Saw mill	-	0	6,300	0	0
	Bark	1	0.50		4,649.25	29.29
Palm oil tree	Fronde	2.604	1	7,540	14,355.86	108.24

There are many routes to produce transportation fuel from biomass e.g. extraction, fermentation, pyrolysis and other thermo-chemical conversion [1]. The production of transportation fuel in Thailand is currently based on the transesterification and fermentation process [2]. The first is used to produce bio-diesel, whereas the latter is for production of gasohol. The general process description for both bio-fuels is shown in Figure 3.

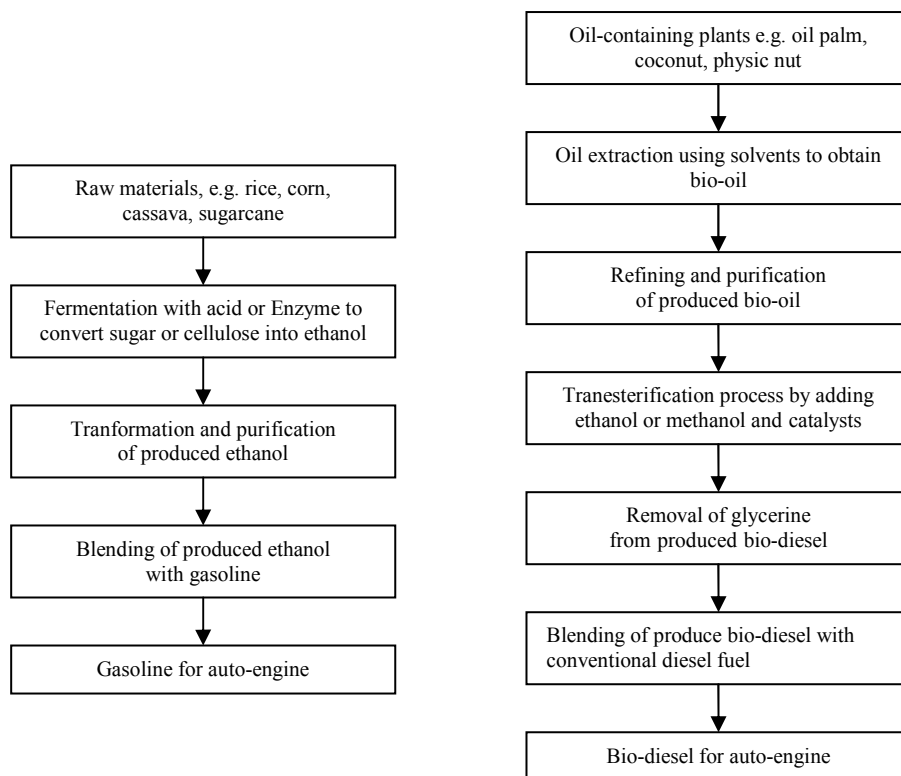


Figure 3 General process description for the production of gasohol (a) and bio-diesel (b) in Thailand

Although both bio-fuels have already been sold in Thailand, there are some disadvantages of these bio-fuels. The main advantages are:

- Both ethanol and bio-diesel cannot directly used in automobiles. They have been blended with the commercial gasoline and diesel, respectively. The ratio of 85% gasoline and 15% ethanol is recommended for gasohol [2] or not more than 5% bio-diesel should be added in conventional diesel for used bio-diesel [1].
- Both renewable transportation fuels can only be derived from the oil- and starch-containing biomass. Lignocellulosic biomass cannot used as feedstock to produce such bio-fuels via these processes with high efficiency [10]
- They also cannot be distributed using existing infrastructure [1].

In this study, the possible processes to produce synthetic diesel that can be directly used in the automobile and existing infrastructure will be theoretically investigated.

2. MATERIALS AND METHODS

Biomass feedstock

All of the agricultural biomass residue in Thailand from Table 1 and the woody biomass from Table 2, including corncob, were used as the raw materials for the theoretical calculation of liquid transportation fuel production. The biomass characteristics are reported by EFE [6] and are presented in Table 3.

Table 3 Proximate and elemental analyses of biomass feedstock

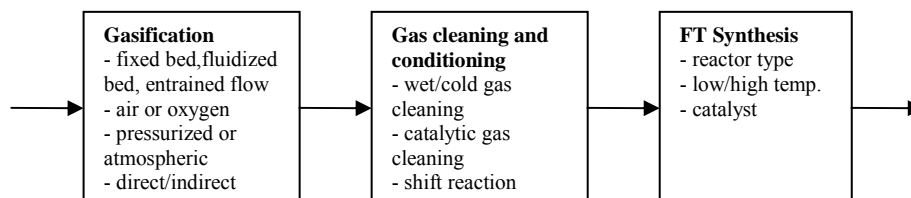
	Bagasse	Cane trash	Rice husk	Rice straw	Cassava rhizome	Corn cob
<i>Proximate analysis (wt% as received)</i>						
Moisture	50.73	9.20	8.20	10.00	59.40	7.00
Volatile	41.98	67.80	58.90	60.70	31.00	70.40
Fixed C	5.86	16.90	19.70	18.90	8.10	21.20
Ash	1.43	6.10	13.20	10.39	1.50	1.40
<i>Elemental analysis (wt% as received)</i>						
C	21.33	41.60	39.10	38.17	18.76	43.70
H	3.06	5.08	4.59	5.02	2.48	5.21
N	0.12	0.40	0.18	0.58	0.32	0.19
O	23.29	37.42	34.70	35.28	17.50	42.50
	Palm oil fiber	Palm oil EFB	Palm oil shell	Rubber wood tree	Eucalyptus tree	Palm oil tree
<i>Proximate analysis (wt% as received)</i>						
Moisture	31.84	58.60	12.00	45.00	50.00	48.40
Volatile	48.61	30.44	68.20	45.70	35.00	38.70
Fixed C	13.20	8.04	16.30	7.71	11.95	11.70
Ash	6.35	2.92	3.50	1.59	3.05	1.20
<i>Elemental analysis (wt% as received)</i>						
C	31.35	15.11	44.44	15.56	13.25	23.89
H	4.57	1.51	5.01	3.19	2.65	3.04
N	0.02	2.57	0.28	0.14	0.19	0.56
O	25.63	19.13	34.70	24.48	20.85	22.91

The production of transportation fuel

To overcome disadvantages of both conventional bio-fuels, the proper two routes, Fischer-Tropsch synthesis via biomass gasification (BG-FT) and the catalytic depolymerisation process (CDP), are taken into account. Both can be considered as the thermochemical conversion of biomass to liquid transportation fuel.

The BG-FT can be separated into 3 sub-processes, biomass gasification, gas cleaning and Fischer-Tropsch process [11], as shown in Figure 4.

At first, the biomass material is converted into the synthesis gas which comprises mainly of hydrogen and carbon monoxide at the elevated temperature between 700-1500°C [1], depending on the type of gasifier and the characteristics of biomass feedstock. This sub-process is called the biomass gasification process. The synthesis gas must be free from tar, particulate and other catalyst-poisoning substances. Therefore, this synthesis gas has to be cleaned and conditioned until it is suitable to be used as feedstock for Fischer-Tropsch reaction. This step is named as the gas cleaning and conditioning process. After the synthesis gas has been cleaned, it can be used as feedstock to produce synthetic diesel in the Fischer-Tropsch process. The FT reaction is a process to convert synthesis gas to a wide range of long chain hydrocarbon product, from LFG, gasoline, naphtha, diesel to wax [11], with the aid of iron- or cobalt-based catalysts under high temperature and high pressure. The produced long chain hydrocarbon is finally distilled, hydro-cracked or upgraded before being used as a liquid transportation fuel.

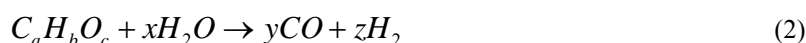
**Figure 4** A schematic of converting biomass to FT-liquids

The maximum amount of liquid fuel from the BG-FT process has been investigated from the stoichiometric chemical equations of both biomass gasification process and Fischer-Tropsch process and the composition of biomass feedstock [12]. The stoichiometric chemical equations of both processes are described as follows:

Biomass gasification with oxygen as gasification agent



Biomass gasification with water vapour as gasification agent



Simple Fischer-Tropsch reaction with $n = 1$



The CDP is the alternative route to produce liquid transportation fuel from biomass. This process is principally based on direct liquefaction of biomass [13-15]. In this process, the long chain hydrocarbons or organic materials have been cracked into light crude oil with the aid of ion exchanged catalysts under a temperature of less than 500°C and atmospheric pressure [13]. An example of a depolymerisation reaction of organic feedstock into liquid transportation fuel is illustrated in Figure 5.

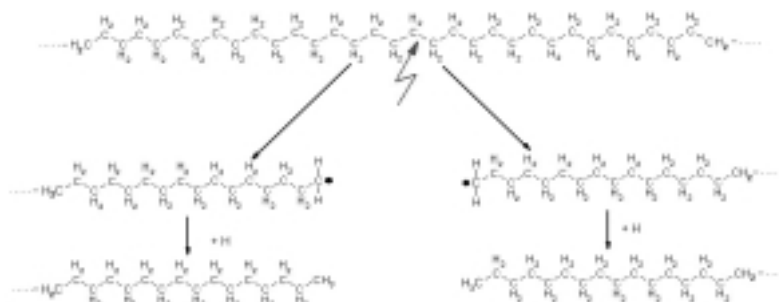


Figure 5 Depolymerisation reaction of organic feedstock into diesel

Since there are no exact chemical equations for the catalytic depolymerisation process, the results of this process can be obtained only from the experimental work. There are many studies for investigation of liquid fuel production form CDP available [13-15]. The results of the experimental work can be summarized as follows.

The experiment was carried out at the reaction temperature of about 370°C at atmospheric pressure at the laboratory scales with a biomass capacity of 1 kg/h. Several types of biomass have been tested to study the mass and energy balance of the process, and the result can be summarized as [13-14]:

Mass: 100 %wt biomass \rightarrow 43 %wt oil + 22 %wt water + 15 %wt coal + 20 %wt gas
 Energy: 100 %e biomass + 5 %e EC \rightarrow 76 %e oil + 20 %e coal + 7 %e gas + 2 %e energy loss

From both mass and energy balances, it can be concluded that the oil yield from the CDP is more than 40% by weight, and the energy efficiency is also more than 70%.

For estimation of the theoretical amount of diesel produced from CDP, the followings assumption are used:

- Energy efficiency of this process is 70% (based on higher heating value). This value is the minimum value from [13].
- Higher heating value of produced synthetic diesel fuel is 42,714 kJ/kg [15].
- Density of produced synthetic diesel fuel is 865 kg/m³ [16]
- Higher heating value of biomass from Thailand is obtained from [6]

3. RESULTS AND DISCUSSION

According to the biomass analysis and equations 1 to 3 in the last section, the results of the maximum (theoretical) liquid fuel production via BG-FT based on 1 kg of biomass is shown in Table 4. In this case both oxygen and water vapor has been used as gasification agent.

Table 4 The maximum amount of liquid fuel production via BG-FT from Thai biomass

Type of biomass	Chemical formula	Max. fuel with O ₂ as agent (g/kg biomass)	Max. fuel with H ₂ O as agent (g/kg biomass)
Sugarcane trash	C _{4.1} H ₆ O _{2.8}	210.00	301.00
Bagasse	C _{3.7} H _{6.4} O ₃	226.80	274.26
Rice husk	C _{4.1} H _{5.8} O _{2.8}	203.42	294.56
Rice straw	C ₄ H _{6.3} O _{2.8}	222.60	301.56
Palm oil fibre	C _{4.2} H _{7.4} O _{2.6}	260.54	373.24
Empty fruit bunch	C _{3.4} H _{4.1} O _{3.3}	146.86	154.14
Palm oil shell	C _{4.4} H _{5.9} O _{2.6}	205.94	331.52
Cassava rhizome	C ₄ H _{6.4} O _{2.8}	225.82	310.52
Rubber wood	C ₄ H ₆ O _{2.4}	227.36	348.46
Eucalyptus	C _{4.1} H _{5.7} O _{2.8}	200.20	280.84
Palm oil tree	C ₄ H _{6.1} O _{2.9}	212.52	289.10

From Table 4, it can be deduced that:

- Biomass, which has higher hydrogen content, can generate more liquid transportation fuel. This is due to the hydrogen content in biomass contributing to promote more hydrogen in synthesis gas compared to biomass with lower hydrogen content.
- The gasification system with water vapor as a gasification agent can produce more liquid fuel than with oxygen as gasification agent because hydrogen in water vapor will increase the amount of hydrogen in synthesis gas.

This means that the amount of liquid fuel depends strongly on the synthesis gas component. The ratio of hydrogen to carbon monoxide in synthesis gas has to be 2:1, as shown in Eq. 3. Besides the composition of biomass and the use of gasification agent, the type of gasifier and operation temperature and pressure also has effects on synthesis gas composition [16]. The special gasifiers used for the production of synthesis gas have been presented together with the synthesis gas composition in Table 5. These gasifiers have been developed in Europe for tar-free synthesis gas production, which can be further used for hydrogen production, FT-synthesis or other production of other chemicals. However, it must be kept in mind that the maximum amount of liquid fuel is calculated using the stoichiometric equations and without any loss conditions. In the actual real process or real plant, there are many losses for example energy loss and friction loss during the gasification process, gas cleaning process, FT-synthesis and also during the upgrading process. The energy efficiency of BG-FT depends on many processes, ranging from the gasification process until the upgrading process. From the work of Boerrigter *et al.* [17], the overall energy efficiency of synthesis gas conversion to final diesel yield (η_{GtL}), has been estimated to be about 71% based

on lower heating value of biomass. The overall energy efficiency of biomass conversion to final diesel yield of 42-50% for pressurized systems and 33-40% for atmospheric systems has been reported by [10]. That means the amount of diesel yield from BG-FT is always less than the result from calculations.

Table 5 Special gasifiers for synthesis gas production [18-24]

	Carbo V	Entrained flow gasifier	CFB (CUTEC)	Blue Tower Gasifier	FICFB (TU Wien)
Total system	Low temp. gasifier and entrained flow gasifier	Pyrolysis and entrained flow gasifier	Circulation Fluidized Bed gasifier (CFB)	Pyrolysis and reforming	Fast internal gasification
1 st stage	Low temp. gasifier at 400-600°C	Flash pyrolysis 500°C	-	Pyrolysis 550-600°C	-
Gasifier	Autotherm entrained flow gasifier with 2 zones: Combustion 1300-1500°C, Gasification 800-900°C P _{atm}	Autotherm entrained flow gasifier ~1300°C and >50 bar	Autotherm CFB with silica sand as bed, >900°C, P _{atm}	Allotherm reforming with ceramic as heat carrier, 950°C, P _{atm}	CFB gasification with 2 zones : Combustion with air 970°C, Gasification 900°C
Gasification Agent	O ₂ /air	O ₂	O ₂ /H ₂ O	H ₂ O	H ₂ O
Gas cleaning	Bag filter, wet scrubber, SO ₂ -removal	Wet scrubber, cooling, SO ₂ -removal	Hot gas filter with ceramic, wet scrubber, carbon adsorber	unknown	Filter, wet scrubber, ZnO adsorber, removal of S und Cl
Gas conditioning	WGS, CO ₂ -removal	WGS, CO ₂ -removal	WGS, CO ₂ -removal	unknown	unknown
<i>Synthesis gas composition (%vol.) after gas cleaning</i>					
H ₂	40.2 (22.1)	27	26.04	53	38-40
CO	39.2 (21.8)	50	29.91	12	22-26
CO ₂	20.4 (11.4)	14	33.69	25	20-22
CH ₄	0.1 (0)	< 0.1	8.8	6	9-11
N ₂	0.1 (44.7)	6.3	0.17	2	1.2-2

Note: The number in the blanket for Carbo V gasifier is the synthesis gas composition, when air is used as gasification agent.

According to calculation of liquid transportation fuel from Thai biomass via CDP, the results of liquid fuel production based on 1 kg of biomass via CDP is shown in Table 6.

Table 6 Amount of diesel product from Thai biomass via CDP

Type of biomass	HHV of biomass (kJ/kg)	Diesel production (g/kg biomass)	Diesel production (l/kg biomass)
Sugarcane trash	16,794	275.22	0.32
Bagasse	9,243	151.47	0.18
Rice husk	15,400	252.38	0.29
Rice straw	13,650	233.70	0.26
Palm oil fibre	13,548	222.03	0.26
Empty fruit bunch	8,969	146.98	0.17
Palm oil shell	18,267	299.36	0.35
Cassava rhizome	7,451	122.11	0.14
Rubber wood	10,365	169.86	0.20
Eucalyptus	8,514	139.53	0.16
Palm oil tree	9,354	153.29	0.18

After the theoretical calculations by using both biomass gasification with integrated Fischer-Tropsch synthesis (BG-FT) and catalytic depolymerisation process (CDP), it can be concluded that, the CDP can provide more diesel output due to its higher energy efficiency (more than 70%), whereas the energy efficiency of BG-FT is only 33-50%. Besides the higher heating value of biomass itself, all the operation parameters and the catalysts will affect the amount and quality of liquid fuel produced from CDP. The effects of these parameters will be investigated in the future. In addition to the higher diesel output, the cost of CDP is also less than the BG-FT which consists of a two step conversion process: biomass gasification and FT-Synthesis.

Advantages of FT-diesel and CDP-diesel are that they are high quality and ultra clean transportation fuel with very low sulphur content and aromatic compounds. The specification of FT-diesel and diesel derived from CDP is illustrated in Table 7, in comparison with petroleum-derived diesel [1, 15]. In addition, the FT-Diesel and diesel derived from CDP can be directly used in the automobiles and existing infrastructure without any adaptations.

Table 7 Specification of FT-diesel and CDP-diesel in comparison to conventional diesel

Fuel specification	FT-Diesel	CDP-Diesel	Conventional diesel
Chemical formula	Paraffin		C ₁₂ H ₂₆
Molecular weight (kg/kmol)			170-200
Cetane number	> 74	63	50
Density (kg/l) at 15°C	0.78	0.865	0.84
Lower Heating Value (MJ/kg) at 15°C	44.0	42.7	42.7
Lower Heating Value (MJ/l) at 15°C	34.3		35.7
Stoichiometric air/fuel ratio (kg air/kg fuel)			14.53
Oxygen content (%wt)	~ 0		0-0.6
Kinematic viscosity (mm ² /s) at 20°C	3.57	10.6	4
Flash point (°C)	72	77	77

For the economic point of view, both synthetic diesel fuels can compete with conventional diesel fuel in the near future, because the possible high crude oil price. The production cost of FT-Diesel and CDP-Diesel is 0.31-0.45 €/liter and 0.23-0.40 €/liter, respectively [1, 25] whereas the crude oil price is about 60.77 €/barrel and it is predicted that the crude oil prices can reach 82.89 €/barrel in next year [26].

4. FUTURE WORK

Although, FT-diesel is more expensive than CDP-diesel, both types of synthetic diesel fuel will be studied in the future. The next step is to carry out the Aspen Plus[®] simulation programme in order to optimize the BG-FT process which can produce the maximum amount of FT-diesel. The parameter such as gasification temperature, gasification agent and also temperature of FT-synthesis will be investigated. This simulation can further be used to construct the pilot plant for BG-FT process. In addition, the laboratory test for CDP will also be performed with the different type of Thai biomass and with variation of operation parameters, e.g. temperature, retention time, amount of catalyst and moisture content of biomass.

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