Penerbit Akademia Baru

Journal of Advanced Research in Engineering Knowledge

Journal homepage: www.akademiabaru.com/arek.html
ISSN: 2600-8440

An upgraded bio oil derived from untreated and treated empty fruit bunches (EFB) by catalytic pyrolysis: A review

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ARTICLE INFO

Article history:
Received 15 June 2018
Received in revised form 14 October 2018
Accepted 20 October 2018
Available online 28 October 2018

Keywords:
Catalytic pyrolysis, empty fruit bunches (EFB), zeolite

ABSTRACT

Catalytic pyrolysis has become promising thermal conversion technique to produce bio fuel from renewable energy resources such as biomass. This is due to the availability of various catalyst used to enhance the quality of bio fuel by eliminating oxygenated compounds via dehydroxylation and decarboxylation, decreasing molecular weight, and altering its chemical structures to resemble those of petrochemical products. For selecting an appropriate catalyst for production of high quality of bio fuel, it is important to have good knowledge of its chemical properties and physical characteristic, along with their role during pyrolysis. It is also important to ensure that the results produced by the optimum process parameters are valid and credible by using design of experiment (DOE). The objective of this paper is to evaluate the current progress and challenges of catalytic pyrolysis process of biomass to aid researchers in selecting the most appropriate catalyst and improve the process of catalytic pyrolysis especially on palm empty fruit bunches (EFB). The catalytic pyrolysis of untreated and treated EFB, type of catalyst, different reactor system and application on design of experiment were investigated. In the last part of this reviewed study point out the potential scope of researches about upgrading a catalytic pyrolysis in the future.

1. Introduction

The thermal catalytic conversion of biomass has received much attention by many researchers to develop method for bio oil upgrading. Catalytic pyrolysis is one of the most promising and prevailing technology to produce high quality liquid fuel [1,2]. The principle of catalytic pyrolysis is to eliminate and substitute oxygen and oxygen-containing functionalities and increasing the hydrogen to carbon ratio of liquid product using a catalyst during the pyrolysis process. In general, the catalysts should be highly active, selective to particular products, resistant to deactivation, readily recycled and low cost to improved efficiency of the valuable product yields [3,4]. Zeolite was identified the popular cracking catalyst in catalytic pyrolysis of biomass by many researchers [5-15]. Modification of zeolite by metal loaded [5,16] and altering the chemical structure [9,17,8] has been actively explored.

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However, there several potential problems when using low grade of feed stocks, inefficiency of reactor system and inappropriate application on design of experiment (DOE).

To overcome this problem, it is important for researchers and developers to deeply understand the principle concept of pyrolysis, role of catalyst in thermal conversion and use a suitable DOE which is easy to use; more flexible, modification and validation, and incorporates an appropriate analysis of pyrolysis data and statistical accuracy of the results. To select a credible catalytic pyrolysis process, it is also important to have good knowledge of the available techniques, biomass upgraded and appropriate catalyst, along with their relative strengths and weaknesses. These aspects of dependable are recommended by most of researchers. The use of catalyst as an aid to shorten the time of reaction, enhance the efficiency of products yield and upgraded the quality of bio fuel derived from biomass.

In this paper, the progress and challenges of the palm empty fruit bunches (EFB) as an alternative fossil fuel was revealed. Followed by the revolution pre-treatment of EFB to become a future potential biofuel feed stock was highlighted. In addition, principle of catalytic pyrolysis of biomass in general was also described to give more understanding about thermal conversion process. Further, progress research of non-catalytic and catalytic pyrolysis of untreated and treated empty fruit bunches (EFB) had also reviewed. Last section provides recommendation for future potential researches about an upgrading the catalytic pyrolysis process to enhance the quality and also quality of the pyrolytic product yields.

2. Empty Fruit Bunches (EFB) As A Feedstock and its Reaction Mechanism

Bio oil derived from pyrolysis of palm EFB is facing various challenges such as the low-grade quality of bio oil produced. It can be described as dark brown, content high oxygenated compounds, high acidity, high moisture, low calorific value, high density, and distinctive odour [19,20]. Many factors should be considered for production of high-quality bio oil such as a biomass with high cellulose content, reactor types that capable to achieve high bio oil yields and rapid char separation techniques to reduce solids contamination in bio oil. In addition, pre-treatment on biomass [19,21–23] and consuming of right catalyst [9,18,24,25] was also important to enhance pyrolysis reaction kinetics by cracking heavy molecular compound into lighter hydrocarbon products.

It is very important to understand about lignocellulosic composition of biomass before undergoing any thermal conversion process. Like most other lignocellulosic biomasses, EFB indicates varying compositions of cellulose, hemicellulose and lignin which is summarized in Table 1. There are three major components of lignocellulosic in EFB which are hemicellulose, cellulose and lignin. In term of element composition, carbon and oxygen content are dominated element while nitrogen and sulphur presence small amount in EFB. In addition, large amounts of volatiles in EFB shows it is a potential biomass that could promote the production of high quantity of bio oil via non-catalytic and catalytic pyrolysis.

Understanding the mechanism of pyrolysis of palm empty fruit bunch (EFB) into bio oil is important to produce high quality of biofuel. Thermal cracking or known as pyrolysis become the most promising technique available to convert biomass into bio oil. The effective pyrolysis reactions involve the successive reaction that possibly occur of dehydroxylation, decarboxylation, isomerisation, decarbonylation, polymerisation, and aromatisation [25].

Table 1
Characteristic of palm empty fruit bunches (EFB) based on literature reviews [26]

Characteristics	Literature values (in range)
Component (wt.%)	
Cellulose	17.1-59.7
Hemicellulose	22.1-48
Lignin	18.1-25
Elemental analysis (wt.%)	
Carbon	43.6-49.07
Hydrogen	5.9-6.41
Nitrogen	0.65-1.41
Oxygen	38.29-49.23
Sulphur	0.10-0.40
Proximate analysis (wt.%)	
Moisture content	4.1-8.96
Ash content	5.36-7.0
Volatiles	65.1-83.86
Fixed carbon	7.5-23.7
HHV (MJ/kg dry)	16.74-18.96

The main reaction mechanisms involve during the primary conversion of biomass suggested by Zhang *et al.*, [24] was illustrated in Figure 1. There are three pathways mechanism reaction involve in biomass conversion which are char formation from monomers into polycyclic aromatic structure and low molecular weight compounds at temperature less than 500 °C. When temperature increase between 500 to 600°C, depolymerization reaction occur. Fragmentation reaction involve at higher reaction temperature which is more than 600°C to produce incondensable gas such as CO and CH_4 including light molecular compounds [24].

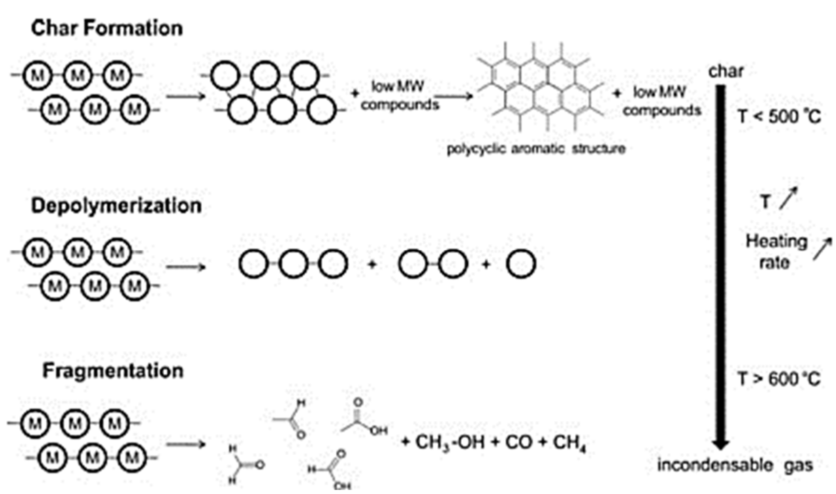

Fig. 1. Three main pathways mechanism involved during the conversion of biomass constituents (M, monomer; MW, molecular weight) [24]

2.1 Pre-treatment of EFB

Bio oil derived from a fast pyrolysis of untreated EFB was found separated in two phases with predominant of tarry organic compounds and an aqueous phase [27] causing difficulties for fuel applications. Poor properties of bio-oils which has high water and oxygen content, high O/C atomic ratio and lower calorific values is not attractive for the alternative production of fossil fuel. Therefore, pre-treatments of EFB have been widely reported to find several effective methods such as washing, acid leaching, torrefaction [28-31] and combination of these pre-treatments [32] in order to enhance properties of this biomass and increase the conversion and pyrolysis product yields.

The minerals (ash) in biomass are knowns to act as a catalyst for pyrolysis process lead to a serious problem such as slagging, fouling, agglomeration, deposition and heating side corrosion in the high temperature system. Pre-treatments of washing and acid leaching using water and various strong acids, respectively, showed the effective method to upgrade the properties of EFB by reducing amount of ash content also known as alkali and alkaline earth metals (AAEMs) in EFB [19,22,23]. Strong acid leaching capable to removed higher amount of AAEMs from biomass and introduced more important impact on physicochemistry structure of biomass comparing to water and weak acid leaching [33].

Previous researches studied the effect of ash reduction on yield and maximum ash level producing a homogenous bio oil. Water washing pre-treatment was performed on EFB to reduce the ash content by varying the amount of water, the particle size of EFB and soaking time. Five different ash contents in the range of 1.03 to 5.43% for unwashed and washed empty fruit bunches (EFB) were used in fast pyrolysis process. They found that 3% of ash content was the maximum amount that should present in the feedstocks that can yield homogenous of bio oil [34].

Recent studied by Sukiran *et al*., [22] found that the washed feedstock with much reduced ash had beneficial effect on its fuel characteristics. Sulpuric acid was identified the possible leaching agent to reduce ash content in the EFB, while washing EFB with NaOH could increase the ash content, thus, lead to high formation of bio char and gas yield [22]. Similar observation was reported on sulphuric acid as leaching agent by other researcher The effect of acid pre-treatment with various concentration of sulphuric acid (H_2SO_4) at ambient temperature and atmospheric pressure on the production of pyrolysis products was studied. The results indicated that maximum oil yield of 46.8% with minimum char yield of 10.1% was achieved by the treatment with 3 M of H_2SO_4. The shorter chain unit of cellulose, hemicellulose and lignin were produced by moderate acid pre-treatment, thus assisting the conversion into bio oil by pyrolysis [35]. Pre-treating the biomass by eliminating AAEMs, limited the competition reaction between primary and secondary reactions during pyrolysis process resulted in upgrading quality of bio oil. Therefore, modification on biomass feedstocks need to be conducted to reduce AAEMs concentration and oxygen content prior pyrolysis process.

Another promising pre-treatment on EFB that has been investigated to enhance the performance of quality pyrolytic product yield was torrefaction. In the absence or minimal of oxygen at temperature between 200 to 300°C on biomass, torrefaction could improve the energy densification of biomass product [36]. Base on literature, most of studies mainly focus on the effect of torrefaction EFB on the biochar product [29–33,37,38]. The beneficial of torrefied EFB are including; the moisture content is reduced hence O/C ratio is reduced which increased the carbon content and calorific value. Furthermore, higher heating value can increase reactivity and ignitibility of biomass during pyrolysis and gasification which important as biofuel feedstock. The torrefied EFB also resistant to fungal degradation due to it is low in moisture content, therefore increased the storage duration [30]. Generally, torrefaction was strongly depend on the chemical constituents and thermal decomposition behaviour of hemicellulose, cellulose and lignin [31].

Another studied on torrefaction of palm EFB in the present of oxygen reported that the mass yield and energy yield still in the range of 85-95% were decreased with increasing temperature and oxygen concentration but was unaffected by biomass size. Thus, it is worthwhile indicating that torrefaction in the presence of oxygen can be carried out without any significant problems with only 7 % of biomass was lost through complete oxidation at 15% oxygen content [29].

On the other hand, there a many researches have been carried out to observe the effect of torrefaction pre-treatment of other biomass on pyrolysis products yield [39-41]. The effect of torrefied cotton stalk on grinding performance, hydrophobicity, heating value and carbon content are greatly improved while the number of functional groups containing oxygen reduced. In addition, they also found that the yield of bio-oil decreases, while the yield of biochar rapidly increased with increasing torrefaction temperature in the range of 220 to 280°C on cotton stalk after pyrolysis process at 500°C [39]. The properties of bio oil such as heating value and pH was improved when the biomass was treated via torrefaction process however, quantity of bio-oil yield was decreased increasing torrefaction temperature [41].

Based on this review study, it is suggested the pre-treatment on biomass via thermochemical and physical process has beneficial effect such as enhanced the calorific value and carbon content but reduced the oxygen content.

3. Catalytic Pyrolysis of Biomass

Catalytic pyrolysis can be divided into two different process based on the positioning of the catalyst in the reactor i.e., in-situ catalytic vapour cracking and in-bed catalytic pyrolysis. During in-situ process, biomass is cracked to produce pyrolytic vapours which pass through catalyst bed, then converter into bio oil, gaseous and char. While, in-bed system, catalyst is mixed with biomass in the reactor during pyrolysis occur. In-situ catalytic pyrolysis is commonly applied due to independently controllable of catalytic temperature and pyrolysis temperature [42]. The catalytic cracking technology capable to produce hydrocarbon bio fuel or valuable chemical feedstock by deoxygenation of bio oil via decarbonylation, decarboxylation and dehydration. This process has gained more attention since catalytic cracking does not require the use of higher hydrogen pressure resulting in low cost operation. Moreover, catalytic cracking seem to be a cheaper method due to such process typically using inexpensive zeolite catalyst under atmospheric pressure [43].

Catalytic pyrolysis is characterized basically on temperature of reaction between 450-600°C, main catalyst involved such as zeolite, metal loaded catalyst, mesoporous material, dolomite and metal oxide and the reaction occurs in inert condition with supplies of inert gases. The products of catalytic pyrolysis are liquid, char and gas. Most of the liquid product derived from catalytic pyrolysis of biomass are phenolic compound, aromatic compound and hydrocarbon. The phenolic compounds are degradation product of lignin in the biomass. While aromatic compounds are produced from a number of difference reactions involving during the pyrolysis process such as cracking, oligomerization, dehydrogenation and aromatization with presence of sufficient amount of strong acid side [44].

Catalytic pyrolysis of biomass over acidic catalysts has attracted significant asttention as a method of promoting the production of aliphatic and aromatic hydrocarbons. Alternatively, low cost catalyst like zeolite has been used in catalytic cracking reaction for converting the oxygenated compounds of bio oil into hydrocarbon under atmospheric pressure [8,10,13]. Zeolite is widely used in catalytic pyrolysis of biomass and HZSM-5 zeolite catalysts were mostly used for catalytic pyrolysis. This process contribute to conversion of oxygenates to furans and aromatics on the Brønsted acid sites. Catalytic pyrolysis of EFB over HZSM-5 showed the selectivity to produce aromatic hydrocarbon via the phenolic pool mechanism [25].

The effect of torrefaction on catalytic fast pyrolysis of corncobs biomass was investigated the torrefied using nanosized HZSM-5 performed in a semibatch-pyroprobe reactor with varied temperature and resident time at atmospheric condition. They found that the optimal torrefaction condition was at light and mild torrefaction (temperature at 210 to 241°C) with resident time of 40 min. The torrefaction can promote an effective thermal pre-treatment for improving the selectivity of BTX (benzene, toluene and xylene). However, the increasing of coke yield and reduction of aromatic yield were observed at severe torrefaction condition (temperature at 270 to 300°C) that could be explained by the serious cross-linking and charring during the torrefaction process.

Previous research developed an integrated process for production of gasoline fraction bio fuels from bio oil under atmospheric condition in the present of HZSM-5 using two steps: one for producing of light olefins by catalytic cracking of bio oil followed by synthesis of liquid bio fuel from light olefins in step two. The biofuel produced from optimize catalytic pyrolysis condition was low in oxygen and benzene content, high RONs (research octane numbers) and high calorific value. This integrated process promising the alternative pathway for production of green gasoline from bio oil of biomass [43].

Further progress in catalytic pyrolysis to achieved maximum of pyrolysis product yield is by optimizing the operation parameters. Design of experiment (DOE) has been applied on catalytic pyrolysis in order to determine the influence of process parameters and optimize operation condition during catalytic pyrolysis process for bio oil production [45-48]. Utilization of Taguchi's Orthogonal Array for optimization method of catalytic pyrolysis of EFB showed that the most significant influence of four reaction parameters were catalyst loading followed by type of catalyst, reaction temperature and nitrogen flow rate. Base on experimental results, the maximum yield of bio oil obtained was 44.05% which closed to the predicted yield with condition of 5% of H-Y zeolite catalyst at temperature 500 °C and nitrogen flow rate of 100 mL/min [47].

Appropriate catalyst and optimum operation process condition is needed to develop an advance cost-effective multifunctional catalyst system [49].Response surface methodology is one of the common DOE used as a tool for optimizing the effectiveness of operating system. There are many types of response surface experimental design such as central composite design (CCD), box-behnken, one factor factorial design, and 3-level factorial design. This experimental design and statistical methods are applied together with a statistical mathematical model for the analysis of responses [48]. Characterization of the optimal catalytic pyrolysis conditions using box-behnken for bio-oil production from brown salwood (Acacia mangium Willd) residues and dolomite used as a catalyst in this reaction was reported. The bio oil yield carried out from catalytic pyrolysis was obtained about 44.78 % with present of 1.0 wt% dolomite catalyst. The role of CaO and MgO in calcined dolomite is to boost decarbonylation and decarboxylation reactions during catalytic pyrolysis, resulted to the improved formation of CO and CO_2 [46].

Suitable catalyst with optimum operation condition of catalytic pyrolysis suggested that product yield and quality of biofuel could be enhanced by applying right model of response surface methodology (RSM).

Table 1
Summary of non-catalytic and catalytic pyrolysis of untreated and treated palm empty fruit bunches (EFB)

Feed	Type of reactor	Catalyst	Temperature	Finding	Ref.
EFB	Continuous pyrolysis reactor	Non-catalytic pyrolysis	350-600 °C	At optimum condition of 530 °C reaction temperature, flow rate of nitrogen 200 cm^3/min and particle size below 1180 µm, about 59.90 % of bio oil was obtained.	[50]
EFB	Fixed-bed reactor	Non-catalytic pyrolysis	400-600 °c	At lower temperature of 400 °C, about 31.34 % of bio oil yield was obtained. When the temperature increased to 600 °C, bio oil yield also increased to 46.67 %. This trend may explain due to decomposition of primary reaction of feedstock and secondary decomposition of bio char at higher reaction temperature, thus enhance the bio oil yield.	[51]

				In terms of chemical compounds in non-.catalytic of EFB, major pyrolysis product was oleic acid (42.88 %), and followed by phenolic compound (16.74 %).	
		5 % of $Ca(OH)_2$, K_2CO_3 and MgO	600 °C	Catalytic pyrolysis of EFB using 5 % of $Ca(OH)_2$ produced higher yield of bio oil compared with K_2CO_3 and MgO. Bio gas yield was found to increase for all three of catalyst when compared with non-catalytic pyrolysis. For catalytic pyrolysis using $Ca(OH)_2$, the main component of phenolic compound was identified about 27.42 % with reducing in oleic acid (7.67 %).	
EFB	Fixed-bed reactor	10 % of CaO (egg shell)	400-550 °C	About 36.6 % of bio oil was produced at optimum catalytic pyrolysis of 400 °C reaction temperature and heating rate of 80 °C/min for about 4 min holding time. When increased the temperature to 550 °C, bio oil was decreased to 4.9 %. Further increased the temperature resulted in reducing on bio oil yield due to secondary cracking reaction of liquid fraction to H_2 and CO gas.	[52]
EFB and EFB treated with NaOH	Auto clave	1 % of Zeolite (synthesis from rice husk)	320 °C	Treated EFB with NaOH produced the highest yield of bio oil about 60 % on catalytic pyrolysis using zeolite synthesis from rice husk. While, about 35 % of bio oil yield was obtained from untreated EFB on similar catalytic pyrolysis condition. Desired chemical compounds such as hydrocarbon, phenol and alcohols were obtained in catalytic pyrolysis which can be used as alternatives for fossil fuel or high valued chemicals. However, undesired compound with poor characteristic as a fuel also produced such as esters, ethers, aldehydes and ketones, during the process.	[53]
EFB	Fixed-bed reactor	Non-catalytic pyrolysis	400-600 °C	The maximum bio-oil yield was obtained from non-catalytic of pyrolysis at 500 °C which about 44 %.	[25]
		HZSM-5, spent fluid catalytic cracking (FCC), bentonite, dolomite, and olivine.	500 °C	Catalytic pyrolysis of EFB produced smaller quantities of bio-oil and larger yield of bio char when compared to non-catalytic and similar pyrolysis condition. This suggests that in the presence of catalyst, bio char was being produced more due to coke formation on the catalyst. The bio-oils obtained from the catalytic pyrolysis of EFB over the spent FCC and HZSM-5 catalysts produced higher amount of gas and a small amount of bio oil during the catalytic. pyrolysis of EFB at 500 °C. In addition, HZSM-5 was identified the most efficient catalyst due to the selectivity to aromatic hydrocarbon compounds, produce a lower oxygen content of bio oil and had a higher heating value (28.44 - 31.18 MJ/kg) compared to bio oil obtained over others catalyst in the range of 16.83 to 27.89 MJ/kg.	
EFB	fluidised fixed bed reactor	Non-catalytic pyrolysis	500 °C	For untreated EFB, about 47.4 % of bio oil yield was obtained from non-catalytic pyrolysis that carried out in fluidised fixed bed reactor.	[22]
EFB Washing with H_2O, H_2SO_4, NaOH				For EFB treated washing with H_2SO_4 produced the highest bio oil yield about 55.6 % using similar reaction condition. EFB washing with H_2SO_4 enhance the carbon content (44.8 wt.%) whereas the oxygen and ash content decreased. These suggested that washing method with a strong acid produced better fuel in terms of calorific value, i.e. 22.5 MJ kg^{-1}	
EFB	Semi-batch stainless steel reactor using	5 % of HZSM-5, HY and Al-MCM-41	300 °C	Untreated EFB yielded higher of bio oil which was about 30 % with lower gas yield (25 %) and 42 % of char yield.	[54]
EFB treated with NaOH + H2O2 and Ca(OH)2 + H_2O_2				Bio oil yield obtained from treated EFB via catalytic pyrolysis (28 %) was lower than untreated EFB. It is due to lower lignin content and disappearance of some important lignocelluloses in the treated EFB contribute to demonstrated lower conversion and thus leaving higher char yield (48 %). They discovered that the bio-oil produced with Al-MCM-41 and HZSM-5 catalyst showed the highest yield of phenol which was up to 90 % and 80% respectively, higher than those produced with HY catalysts (70 %), as well as without catalyst (66 %).	

EFB	Tube furnace reactor	H-Y catalyst (range from 1 to 12%)	500 °C	Design of experiment was applied based on Taguchi's L9 Orthogonal Array with 9 runs of experiment and assisted by statistical analysis. The liquid yield of 44.05 % was obtained at optimum condition of catalytic pyrolysis using 5 % of H-Y catalyst loading at temperature of 500 °C and with nitrogen flowrate of 100 mL/min.	[47]

4. Conclusion and Recommendation

This study reviews the catalytic pyrolysis of untreated and treated EFB in the presence of various of catalyst including zeolite (HZSM-5, HY and Al-MCM-41), metal oxide (CaO and MgO) and Alkali and alkaline earth metal catalyst (Ca(OH)2 and K2CO3) to produce high quality of biofuel from renewable energy resources. From this review, the utilization of metal oxide catalyst on catalytic of untreated and treated EFB produce dominantly phenolic compound which has predominant function as chemical feedstock. Whereas, the consumption of zeolite in catalytic pyrolysis for untreated and treated EFB generated mostly aromatic hydrocarbon and reduced the acidity of bio oil which make it suitable as a biofuel. Furthermore, the study on reusability of the catalyst and regeneration of the catalyst active side are highly recommended as a future research in order to increase the efficiency of catalytic pyrolysis process. In addition, application of doped zeolite with transition metals such as nickel and cobalt could promote the efficiency of catalyst during catalytic pyrolysis process. The future challenge is to increase the ability of the catalyst, thus, the quality and quantity of biofuel can be enhanced for intermediate chemical feedstocks, industrial application and transportation.

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