



Review

A review on conversion of biomass to biofuel by nanocatalysts

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HIGHLIGHTS

- >Significant improvements in biomass conversion using nanocatalysts.
- >Feasibility of utilization milder operating conditions by using nanocatalysts compared to the bulk catalysts.
- >The role of nanocatalysts to overcome some challenges in biomass conversion, improving the products quality.

GRAPHICAL ABSTRACT

Products from nanocatalytic conversion of biomass



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ABSTRACT

The world's increasing demand for energy has led to an increase in fossil fuel consumption. However this source of energy is limited and is accompanied with pollution problems. The availability and wide diversity of biomass resources have made them an attractive and promising source of energy. The conversion of biomass to biofuel has resulted in the production of liquid and gaseous fuels that can be used for different means methods such as thermochemical and biological processes. Thermochemical processes as a major conversion route which include gasification and direct liquefaction are applied to convert biomass to more useful biofuel. Catalytic processes are increasingly applied in biofuel development. Nanocatalysts play an important role in improving product quality and achieving optimal operating conditions. Nanocatalysts with a high specific surface area and high catalytic activity may solve the most common problems of heterogeneous catalysts such as mass transfer resistance, time consumption, fast deactivation and inefficiency. In this regard attempts to develop new types of nanocatalysts have been increased. Among the different biofuels produced from biomass, biodiesel has attained a great deal of attention. Nanocatalytic conversion of biomass to biodiesel has been reported using different edible and nonedible feedstock. In most research studies, the application of nanocatalysts improves yield efficiency at relatively milder operating conditions compared to the bulk catalysts.

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1. Introduction

The demand for energy is increasing in the world due to the rapidly growing global population and urbanization. Throughout history, mankind

has used wood as a source of producing energy. After the industrial revolution, the main source of energy shifted to fossil fuels. The accurate amounts of the world's total fossil fuel reserves are not known. However, it has been forecasted by the International Energy Agency that the global peak

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in oil production will be between 1996 and 2035 (Kumar et al., 2009; Hansen et al., 2010; Liu et al., 2012; Demirbas, 2008; Sinag, 2012; Shirazi et al., 2013; Hamze et al., 2013a, 2014b). Furthermore, the increase in crude oil prices and the pollution caused by petroleum-based energy sources have created serious environmental problems, e.g. global warming. Such concerns about fossil fuels have led to the utilization of alternative energy sources (Dominik and Janssen, 2007; Demirbas, 2008). The primary alternative sources of energy systems that can replace fossil fuels are water, wind, solar energy, and biomass. Currently biomass is gaining a great deal of attention in terms of supplying the world's energy demands. Due to its availability and environmentally friendly nature such as causing no net increase in carbon dioxide levels and producing very low amounts of sulfur, biomass energy is believed to contribute one half of the total energy demand in industrial countries by 2050. Annually, approximately 27 billion tons of CO₂ is emitted from the burning of fossil fuels, and this is predicted to increase about 60% by 2030. Therefore, using bio-derived fuels is crucial to reducing the carbon footprint (Demirbas, 2008).

Biomass energy is supplying about 10-15% (or 45± 10 EJ) of today's demand. Biomass feedstock include a broad range of organic material such as wood, wood-based energy crops, corn stover, grass, algae, wheat straw, rice straw, corn, miscanthus, nonedible oils, green and wood landfill waste, animal fats, waste frying oils, agricultural residues, municipal wastes, forest product wastes, paper, cardboard and food waste. Most biomass is produced through photosynthesis. The photosynthesis yield of approximately 720 billion tons per year, make the largest organic raw material cellulose resource in the world (Demirbas, 2008; Luo and Zhou, 2012). In general all kinds of biomass can be used as feedstock including starchy, triglyceride and lignocellulosic feedstock. Biomass can be converted to biofuels and biopower via thermochemical and biochemical processes. Thermochemical conversion is a significant route for producing products such as bio-methanol, biodiesel, bio-oil, bio-syngas and biohydrogen. Biochemical conversion routes produce liquid or gaseous fuels through fermentation or anaerobic respiration. The production of biofuels through thermochemical conversion processes with a broad range of technologies has drawn the most attention in the world. The main advantage of thermochemical processes for biomass conversion in comparison to other methods such as biochemical technologies is the feedstock used (Mitrovi et al., 2012; Kumar and Tyagi, 2013; Kumar et al., 2009). There are three main routes for biomass' thermochemical conversion including combustion, gasification and pyrolysis. Combustion is the most direct and technically easiest process which converts organic matter to heat, carbon dioxide and water using an oxidant. Gasification of biomass is a heating process within the presence of an oxidant produces a mixture of carbon monoxide and hydrogen referred to as synthesis gas (syngas) by partial oxidation. Gasification has many advantages over combustion. It can use low-value feedstock and convert them into electricity and also vehicle fuels. Within the forthcoming years, it will serve as a major technology for complementing the energy demands of the world (Alonso et al., 2010; Sinag, 2012).

Pyrolysis is a thermal heating of materials in the absence of oxygen, which produces three forms of products including gases, pyrolytic oil and char. Pyrolytic oil, also known as "tar or bio-oil", which is viscous, corrosive, relatively unstable and chemically very complex, cannot be used as transportation fuel directly due to its high oxygen value (40-50 wt%), high water content (15-30 wt%) and also low H/C ratios. Biomass gasification/pyrolysis is one of the promising technologies used for converting biomass to bioenergy (Hansen, 2010; Liu et al., 2010; Aradi et al., 2010a).

One of the most important challenges of the 21st century is the use of nanoscience in the development of sustainable and renewable energy production schemes. In the first decade of the current century, the formation of new fields in catalyst science, named nanocatalysis, has attracted everyone's attention. In general having a large surface to volume ratio of nanoparticles compared to bulk materials, makes them excellent potential catalysts (Aravind and Jong, 2012; Malik and Sangwan, 2012; Kim et al., 2013). The effect of changes in acidic properties, type of metal content and porosity of catalysts are widely known in biomass conversion. However to improve the products' quality, new types of catalysts have been developed. The catalyst utilization, blending of biomass with coal before firing to

improve the quality of products and optimization of the experimental conditions are some important attempts. Also in such applications, increased surface area nanoparticles are extremely attractive candidates (Liu et al., 2010; Wilcoxon, 2012).

There are several methods to prepare nanosized materials. These materials may be used directly or in the form of supported nanoparticles on solids such as oxides, carbon or zeolites. Some usual methods for nanocatalysts preparation are impregnation, precipitation, chemical vapor deposition, and electrochemical deposition. Precipitation and impregnation methods are simple, cheap, and well-studied but it is difficult to control the size of particles. Chemical vapor deposition is widely used in the electronics industries but it is an expensive method. Electrochemical deposition is an inexpensive method that does not need high temperature and concentration. This method would allow a good control on size and chemical properties of the deposited nanomaterials but usually forms one dimensional nanomaterials (Liu et al., 2010; Aradi et al., 2010a; Wilcoxon, 2012). In most research, impregnation and precipitation methods have been used for biomass catalysts preparation. Meanwhile, nanoparticles properties usually adjust by changing synthesis parameters such as pH of the solution, concentration, the reducing agent, and calcination temperature (Pleissson et al., 2012).

Recent catalyst developments have led to the upgrade of biomass gasification processes to increase the syngas production and reduce the tar formation. In catalytic biomass liquefaction the main aims are to increase liquid yield and quality of products. Furthermore, nanocatalyst characteristics, such as high catalytic activities and high specific surface area have helped overcome some limitations on heterogeneous catalysts for their application in biodiesel production from biomass. In this paper the latest progress in nanocatalytic conversion of biomass has been reviewed. However, research studies have not been extended in all biomass conversion fields.

2. Conventional technologies for biomass to biofuel conversion

The process of refining lignocellulosic feedstock to hydrocarbon biofuels can be divided into two general parts. Whole biomass is deconstructed to provide upgradeable gaseous or liquid platforms. This step is usually applied through thermochemical methods to produce synthesis gas (by gasification) or bio-oils (by pyrolysis or liquefaction), or through the hydrolysis route to provide sugar monomers that then deoxygenated to form upgraded intermediates. Thermochemical conversion process is a major method of biomass upgrading for biofuels production, offering a wide range of potential technologies (Hansen et al., 2010). In the following section gasification and direct liquefaction processes have been described as two main thermochemical conversion methods.

2.1. Gasification

Gasification processes provide a competitive route for converting various, highly distributed and low-value lignocellulosic biomass to synthetic gas for generation of a broad sort of outputs: electricity, heat and power, liquid fuels, synthetic chemicals as well as hydrogen production (H₂). The importance of gasification is that it is not constrained to a particular plant-based feedstock, and thus any lignocellulosic biomass can be considered appropriate (Luo and Zhou, 2012; Demirbas, 2008). Gasification of biomass is classified into two different ways, Low-temperature gasification (LTG) and high-temperature gasification (HTG). Production of hydrogen and synthesis of gas conducted through the LTG process is an attractive method, especially for low calorific value biomass, such as livestock manure compost and waste activated sludge. The advantages of LTG process is its easiness and efficient operation while avoiding ash problems such as sintering, agglomeration, deposition, erosion and corrosion. Moreover the tar components in LTG include lighter hydrocarbons which are different from the ones used in the HTG process (Ozaki et al., 2012). Advanced gasification processes are currently being investigated for co-production of liquid fuels in research activities and also in pilot plant scales.

The gasification process includes a sequence of interconnected reactions as it can be seen in Figure 1. The first step includes a quick drying process. Fast pyrolysis takes place in the second step which is a thermal conversion to char and gas products. The final step is gasification, namely, partial oxidation reaction between pyrolysis production and oxygenant. In this process the char is oxidized with an oxygen source (Luo and Zhou, 2012; Bridgwater, 2003;

Nordgreen, 2011). The most frequently used oxidants for gasification process are pure O₂, air, CO₂, steam or a mixture of these components (Nordgreen, 2011).

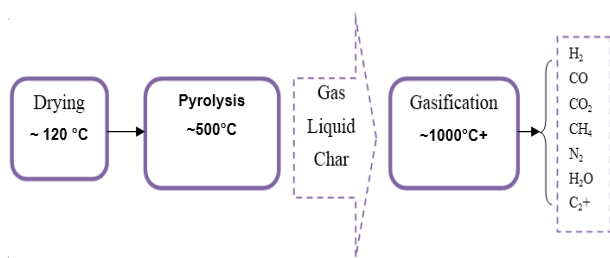


Fig.1. Gasification steps.

The gasification products mainly consist of carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), methane (CH₄), and water (H₂O). During the gasification process, part of the biomass is converted to char particles, tars, and ash instead of syngas. Reduction and conversion of char and tar is one of the major issues in biomass gasification which also increase syngas yield and overall conversion efficiency. The produced syngas quality depends on many factors such as raw material composition, water content, temperature, heating rate, type of gasifier, and oxidation of pyrolysis products. Predicting the exact composition of gasifier products is difficult. One of the methods for theoretically gas composition determination is obtained by using the water-gas equilibrium concept at a given temperature (Kumar et al., 2009; Sinag, 2012; Luo and Zhou, 2012; Asadullah, 2014; Nordgreen, 2011).

Some of the major gasification reactions are as follows:

Exothermic Reactions: (Eq. 1-4)

Oxidation:



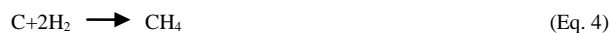
Partial oxidation:



Water gas-shift (WGS):

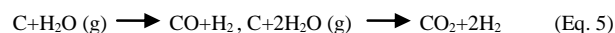


Methanation:



Endothermic Reactions: (Eq. 5 and 6)

Water gas reaction:



Boudouard reaction:



Heat can be provided directly or indirectly to satisfy the necessities of the endothermic reactions. Pyrolysis and gasification reactions will be conducted in a single vessel in directly heated gasification. The required heat for the endothermic reactions can be provided by using air or oxygen as an oxidant,

which combusts a portion of the biomass (Eqs. 1, 2). High purity syngas (i.e. low quantities of inerts like N₂) is extremely beneficial for fuels and chemicals synthesis since it will reduce the size and cost of downstream equipment (Ciferno and Marano, 2002).

The transformation of biomass into hydrogen rich gas provides a competitive means for producing energy and chemicals from renewable resources. Hydrogen production is very important for solving two major energy problems including reducing dependence on petroleum and reducing pollution and greenhouse gas emissions (Rapagna et al., 1998). Tar elimination and CO conversion to levels less than one volume percent by means of the WGS reaction is important for hydrogen production. Producing hydrogen from biomass consists of multiple reaction steps. In the production of high purity hydrogen, the reforming of fuels is followed by two WGS reaction steps, and the final steps are carbon monoxide purification and carbon dioxide removal. Steam gasification processes appear to be optimum candidates which provide an economical, reliable and convenient process for extracting hydrogen from the produced gas. During the steam gasification process, the chemical energy of biomass can be converted into enriched hydrogen syngas containing up to about 50% by volume of hydrogen on a dry basis. Steam can be achieved from the dehydration reactions of crop residues or from an external source. Steam can react with carbon monoxide to produce hydrogen and carbon dioxide. WGS reaction is the principle reaction in the steam gasification system (Chang et al., 2011; Rapagna et al., 2002; Asadullah et al., 2002). Hydrogen can also be produced from biomass by pyrolysis. Biological technologies for hydrogen generation (biohydrogen) provide a wide range of routes for producing hydrogen. Moreover biological processes are considered to be more environmentally friendly and less energy intensive. In general, biomass gasification and the subsequent production of synthetic fuels (diesel fuel, methanol, dimethylether, etc.) requires complex and more expensive technologies compared to conventional petrochemical processes or current direct liquefaction. Therefore it is essential to ensure about the economic viability of biomass gasification plants (Demirbas, 2008; Hansen et al., 2010).

2.2. Direct Liquefaction

Biomass can be converted to liquefied products through combined physical and chemical reactions, the technology being called direct liquefaction. In these processes the biomass macromolecules are decomposed to small molecules through heating and sometimes in the presence of a catalyst. Direct liquefaction may be divided into pyrolysis and liquefaction methods. Although both are thermochemical conversion methods, their operating conditions are different. The operation temperature in the liquefaction method is lower (250-325°C) but the operation pressure (5-20MPa) is higher than that of pyrolysis. In pyrolysis, unlike liquefaction, it is necessary to dry biomass before feeding (Xu et al., 2011).

2.2.1. Liquefaction

Two main routes can be considered industrially for the liquefaction of biomass to bio-oils and these include, hydrothermal liquefaction, and catalytic liquefaction (Vertes et al., 2010). Hydrothermal liquefaction is based on the superior properties of water at higher temperatures and pressures. The reactivity of biomass is considerable in water especially under hydrothermal conditions. Biomass consists of components with polar bonds which are attacked by the polar molecules of water. At elevated temperatures and pressures these attacks are more severe. As a result, hemicellulose and cellulose are hydrolyzed very quickly at these conditions (Kruse and Dinjus, 2007). Hydrothermal liquefaction has another important advantage. Usually all biomass sources are wet and it is possible that their water content be at a range of up to 95wt. %. In most biomass upgrading methods it is necessary to dry feeds before processing. In hydrothermal liquefaction conversions of biomass perform with its high water content. The water content of the biomass not only is not a disadvantage but it is also useful by reducing the process' required fresh water. Using water as both reactant and solvent in the liquefaction has some other benefits as well. The degradable products of the process are completely soluble in water under elevated temperatures and pressures, which prevent any polymerization. In addition, no solid products, such as coke and char, are formed because water acts as both a reactant and solvent in hydrothermal liquefaction. Water in liquefaction has another

important advantage. It is an economic and environmentally friendly solvent, because it will not produce pollution. Mixed solvents (ethanol-water) (Liu et al., 2013) and also other pure solvents (ethanol) (Zheng et al., 2013) have been used in thermochemical conversion of biomass. However, these solvents increase the operating costs of the biomass conversion.

Catalytic liquefaction is similar to hydrothermal liquefaction. However, using a catalyst brings some advantages to the biomass process. Catalyst reduces the residence time and operating temperature and pressure. Catalyst has useful effects on hydrothermal products, it increases liquid products and reduces gaseous one. Also a catalyst can improve liquid products quality (Vertes et al., 2010). As an instance, hydrothermal liquefaction of a microalgae with heterogeneous catalysts showed improvements in products quality (Duan and Savage, 2011). Different heterogeneous catalysts (Pd/C, Pt/C, Ru/C, Ni/SiO₂-Al₂O₃, CoMo/ γ -Al₂O₃ (sulfide), and zeolite) have been used in hydrothermal liquefaction of the microalgae *nannochloropsis* sp., at 350°C. It was seen that the crude bio-oils produced from liquefaction with these catalysts, except zeolite, flowed easily and were much less viscous than the biocrudes of noncatalyzed liquefaction.

2.2.2. Pyrolysis

Thermal, anaerobic decomposition of biomass at temperatures of 377-527°C is called pyrolysis. A temperature of at least 400°C in pyrolysis process is needed to completely decompose the organic structure of the biomass into monomers and oligomers fragments. The noncondensable portion of pyrolysis products rise by increasing temperature to above 600°C. Pyrolysis operations are based on the size of biomass feeds and are divided into two main processes, slow pyrolysis and fast pyrolysis. The slow pyrolysis can disport to conventional charcoal production and intermediate pyrolysis (Vertes et al., 2010). In conventional charcoal production, large pieces of wood are slowly heated to 400°C for a long time (up to 18 hr). The sole product of such process is charcoal when wood was used as a raw material, in the conventional kilns. However, in large retorts with capacities of 100m³ and more, which is used in conventional industrial charcoal production, non-solid products are also achieved. Refining facilities are combined with pyrolysis units to collect and condense gas products. Nevertheless, more than 65% of pyrolysis products are solid (charcoal) and less than 20% are liquid, in conventional charcoal production (Luo and Zhou, 2012; Henrich, 2005).

Intermediate pyrolysis differs from conventional charcoal production in terms of biomass residence time. Wooden feeds are entered into the screw tubular kiln and moved forward by screw rotation. The pyrolysis temperature of 380-400°C is initiated in the kiln by transferring heat from the wall of the kiln, shaft of the screw and also heat carriers. The carriers are balls of various materials with small size. With such heat transfer arrangements, the biomass heated faster than in conventional charcoal production but not as quickly as fast pyrolysis, which is why this process is called intermediate. Another difference between these two pyrolysis methods is related to the products quality. The solid portion of intermediate pyrolysis reduced to about 35%, while the liquid products increased to more than 45% (Schnitzer et al., 2007).

In fast or flash pyrolysis grained biomass with less than 3mm diameter is converted to a combustible liquid fuel in one simple step. The dry feed (less than 20% moisture content) quickly mixes with grainy heat carrier of sand, steel shot, or etc. at approximately 500°C. More than 70% of pyrolysis products are condensed to liquid due to their fast heating and vapor condensation of less than two seconds. The pyrolysis condensates show some hydrophilic behavior caused by their high oxygen content, up to 45%. This behavior makes some problems when these condensates mix with usual hydrocarbon fuels or form two phase liquids. However, this may be solved by mixing the condensates with methanol or ethanol. Furthermore, more oxygen content means lower energy content that is not desirable. One method of reducing oxygen in organic tar is increasing water in the reactor which means entering excess hydrogen in reaction. But the laboratory experiments did not provide efficient results. Another promising method is catalytic deoxygenation of hot stream of biomass pyrolysis products (Xu et al., 2011; Vertes et al., 2010).

In a research work (Malik and Sangwan, 2012) fast pyrolysis products have been used to generate electricity. It is shown that generation of electricity by pyrolysis products is more beneficial than that of any other biomass conversion method in the long term and has a lower cost. In a recent work macroalgae powder has been converted to bio-oil by fast pyrolysis

method in a free fall reactor. Macroalgae (*Enteromorpha prolifera*) has been converted into bio-oil by this process at a temperature range of 100-750°C. Characteristics of the resulted bio-oil were investigated and seen that the average heat value and oxygen content were 25.33 MJ kg⁻¹ and 30.27wt. % respectively (Zhao et al., 2013).

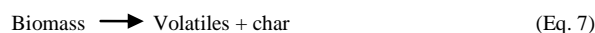
3. Application of nanocatalysts in biofuel production

3.1. Nanocatalysts for biomass gasification

In biomass gasification, preventing tar and char formation is an important issue. Tar is a complex mixture of condensable hydrocarbons including aromatic compounds of single ring to 5-ring along with other oxygen containing hydrocarbons and complex polycyclic aromatic hydrocarbons (PAHs). The boiling temperature of tar is high and it condenses at temperatures below 350°C which creates major problems such as corrosion or failure of engines as well as blockage of pipes and filters. Tars may also act as poison for catalysts. Biomass chars are highly disordered carbonaceous materials with a short-range polycrystalline structure which consist of small aromatic structural units (Asadullah et al., 2002; Li et al., 2008; Luo and Zhou, 2012; Duman et al., 2013a, 2014b; Nordgreen et al., 2011). Two main approaches employed for controlling the production of tar are, including treatments inside the gasifier (primary methods) and hot gas cleaning after the gasifier (secondary methods). Although the secondary methods are effective, primary methods are also gaining much attention because of economic benefits. The most important parameters in the primary methods are including temperature, gasifying agent, equivalence ratio, residence time and catalysts which have significant effects on tar formation and decomposition. The primary methods have not been applied commercially because they are not still fully understood (Balat, 2009; Luo and Zhou, 2012).

The effect of catalysts on gasification products is very important. Catalysts not only reduce the tar content; but also improve the quality of gas products and the conversion efficiency. The presence of a catalyst decreased the char yield during the final step of the gasification process while it increased the char formation during the volatilization stage (Balat, 2009; Aradi et al., 2010a, 2011b). The successful gasification catalysts have some criteria including being effective at removing tars, being resistant to deactivation as a result of carbon fouling or sintering, can easily be regenerated and are inexpensive (Sutton et al., 2001; Wilcoxon, 2012; Aravind and Jong, 2012).

Char formation during the pyrolysis step of gasification can be expressed by the following equation (Eq. 7):



Depends on using steam, oxygen or CO₂ as gasification agent, conversion of the residual chars can be presented sequentially as follows (Duman et al., 2014)(Eq. 8-10):

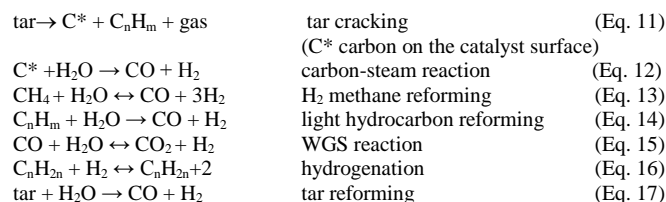


Potassium, sodium and calcium have been found to be the most effective catalysts for promoting char gasification in steam or carbon dioxide media. There may be other metallic species beneficial for biomass conversion, although some elements present in waste biomass may prevent char gasification by poisoning the catalysts (Nzihou et al., 2013).

Catalytic tar cleaning is potentially attractive because no additional input energy is necessary. The important reactions during tar reduction include steam reforming, dry reforming, thermal cracking, hydrocracking, hydro reforming and WGS reactions (Anis and Zainal, 2011; Han and Kim, 2008). The proposed reactions are as follows (Nordgreen, 2011) (Eq 11-17).

In general catalysts for tar conversion are classified into mineral or synthetic. Mineral includes calcined rocks, olivine, clay minerals and ferrous

metal oxides. Transition metals, activated alumina, alkali metal carbonates, FCC catalysts and chars are the main synthetic catalysts.



Tar conversion by using dolomite, nickel-based and other catalysts such as alkali metals at elevated temperatures of typically 800-900°C achieved near 99%. MgCO₃CaCO₃ (Dolomite) is a magnesium ore widely used in biomass gasification. The tar content of the produced gases during the biomass conversion process is significantly reduced in the presence of Dolomite (Sutton et al., 2001; Han and Kim, 2008; Nzihou et al., 2013; Asadullah, 2014). However, dolomite catalysts are efficient in tar cracking; they have some disadvantages such as sensitivity to elevated pressure and thermal instability which leads to loss of surface area due to sintering (Nordgreen, 2011).

Nickel-Based Catalysts are very effective for the catalytic hot gas cleanup during biomass gasification. Elimination of tar is also achieved by Ni-based catalysts with a high rate. Moreover Ni-based catalysts have been used for the production of hydrogen-rich product gas (Balat et al., 2009; Sinag, 2012). Anis and Zainal (2011) reported that among all catalysts for converting tar into fuel gas, nickel catalysts are the most efficient ones. The stability of nickel catalysts increased with co-impregnation of nickel on mineral catalysts (olivine, dolomite, and zeolite). Even if nickel catalysts have a remarkable effect on tar conversion, it may not be recommended for applications in atmospheric biomass gasification due to its high costs and severe risk for deactivation via sulphur chemisorption and carbon deposition (Nordgreen, 2011).

Alkali metals such as lithium, sodium, potassium, rubidium, and cesium can be used directly as catalysts in the form of alkali metal carbonates or supported on other materials such as alumina and silica. Addition of alkali metals to biomass can also be achieved by impregnation. These metals are highly reactive. Alkali metal catalysts lead to an enhancement in the biomass gasification reactions, especially for char formation reactions. The presence of Na₂CO₃, K₂CO₃ or CsCO₃ as catalyst in biomass steam gasification decreased the carbon conversion degree to gas with an increase in the rate and total amount of produced gas (Sutton et al., 2001; Han and Kim, 2008; Basker et al., 2012; Nzihou et al., 2013; Asadullah, 2014).

In recent years, nanomaterials have obtained extensive interests for their unique properties in various fields in comparison with their bulk counter parts. Among the nanocatalysts for biomass gasification, nano-sized NiO (nano-NiO) particles have received a great deal of attention for their catalytic properties. In specific, supported catalyst can be prepared by loading nano particles of NiO on the surface of distinct carriers (such as alumina) which can be more economic (Li et al., 2008a). Li et al. (2008b) investigated the effect of nano-NiO particles and micro-NiO particles as catalysts on biomass pyrolysis. They obtained char yield results for both catalysts and compared the results with the pyrolysis process without using catalysts. Based on the presented data in Table 1, the decomposition of cellulose in the presence of micro-NiO was 10°C lower than that of the pure cellulose, while the decomposition of cellulose with nano-NiO started at 294°C, which was 19°C lower than that of the pure cellulose. The final char yield (5.64 wt. %) was further decreased compared to when micro-NiO particles were applied. They proved the effectiveness of nano-NiO catalysts in pyrolyzing of biomass at a relatively lower temperature.

The results of using nano-Ni catalyst (NiO supported on gamma alumina) in direct gasification of sawdust demonstrated that this catalyst can considerably improve the quality of the produced gas while significantly eliminating tar production (Li et al., 2008a, b).

Aradi et al. (2010) examined the organometallic nanocatalysts of Ni compound and Ni₃Cu (SiO₂)₂ nanoalloy catalyst for biomass gasification. The results showed a significant increase in H₂ production which is well suited for

further processing such as Fischer-Tropsch. Their findings revealed that the nanoalloy catalyst increased biomass conversion efficiency at relatively low gasification temperatures (Aradi et al., 2010a). Other nanocatalysts that have been used in biomass gasification are nano-ZnO and nano-SnO₂ structures. Sinag et al. (2011) have shown that nano-ZnO is an effective catalyst for low temperature WGS reaction, while nano-SnO₂ is an effective catalyst for high-temperature WGS reaction during the cellulose gasification in hot compressed water. As it can be seen in Table 2, results showed a remarkable effect for nano-ZnO on cellulose conversion at 300°C while nano-SnO₂ was an effective catalyst for the cellulose conversion at 400-500°C. The data presented in Table 2 has been obtained based on the information reported by Sinag et al. (2011).

Table 1

Comparison of the char formation in cellulose pyrolysis process using nano-NiO, micro-NiO catalysts and without using catalyst (Li et al., 2008b).

Catalyst	Initial decomposition temperature (°C)	Char yield
Without catalyst	313	6.14
Micro-NiO	303	6.09
Nano-NiO	294	5.64

Table 2

Comparison the effects of bulk and nanocatalysts of ZnO and SnO₂ for cellulose conversion at different temperatures.

Temperature (°C)	Conversion%			
	Nano-ZnO	Bulk ZnO	Nano-SnO ₂	Bulk SnO ₂
300	92.4	83.0	71.0	64.0
400	83.2	83.0	88.2	75.2
500	89.4	83.0	88.4	76.6
600	86.8	75.0	84.2	78.8

The gaseous species obtained at 300°C in the presence of bulk and nano-ZnO mainly consisted of CO₂ and H₂, which revealed the progress of WGS at lower temperatures. The rate of WGS in the presence of nano-ZnO is faster in comparison with the nano-SnO₂. They found that larger surface areas of nano-ZnO enhanced the WGS reaction. Based on a research that used nano zinc-based oxides as catalyst for conversion of glucose into H₂ in supercritical water (SCW), it was found that the existence of both H₂O₂ and ZnO catalysts in the reactor enhanced hydrogen production (Sinag et al., 2011). Hao et al. (2005) investigated tar removal efficiency using CeO₂ particles, nano-CeO₂ and nano-(CeZr) xO₂ catalysts during the cellulose and sawdust gasification process. The experimental results showed a higher activity for the nano-(CeZr)xO₂ catalyst compared to the bulk and nano-CeO₂ (Han and Kim, 2008). The same results for efficient performance of nanoalloy catalysts were obtained by Aradi et al. (2010). The available researches on nanocatalysts in biomass gasification are very limited.

3.2. Nanocatalysts for biomass liquefaction

Alkaline salts, Na₂CO₃, KOH and so on, are commonly used as homogenous catalysts in liquefaction processes (Duan and Savage, 2011). The effects of some other catalysts on the liquefaction of biomass have also been investigated, such as NaHCO₃ (Sun et al., 2010), Ca (OH)₂, Ba (OH)₂, FeSO₄ (Xu and Lad, 2007). The heterogeneous catalysts have been used in catalytic conversion of biomass. Different heterogeneous catalysts Pd/C, Pt/C, Ru/C, Ni/SiO₂-Al₂O₃, CoMo/γ-Al₂O₃ (sulfided), zeolite (Duan and Savage, 2011), and Fe (Sun et al., 2010) have been studied in conversion of the biomass. In catalytic hydro conversion of biomass, liquid catalysts have the advantage of being mono dispersed in reaction mixtures. In other words, solid catalysts have the superiority of higher catalytic activity in addition to being easily separated from the products. Acid-functionalized paramagnetic nanoparticles are promising materials for use in catalytic hydro conversion of

biomass. These functionalized nanoparticles can easily separate and be recycled in the catalytic hydro conversion process. Nanocatalysts have some other advantages which make them attractive for use in biomass to liquid (BTL) processes. Having the fluid solution characteristics, mono dispersed nanocatalysts have excellent accessibility to the oxygen atoms of the cellulose ether linkage (Guo et al., 2012). Conversion of biomass to liquid compounds such as paraffinic, naphthenic and aromatic hydrocarbons can supplement part of the worldwide petrochemical demand. Although use of nanocatalysts in the catalytic conversion of biomass to liquid chemicals has had several advantages; most of the research attention has been paid to conversion of biomass to biodiesel. Having relatively high prices, diesel fuel is in large demand in today's world. So an individual subsection has been assigned to nanocatalytic conversion of biomass to biodiesel. There are very limited studies on the conversion of biomass to other bio- oils. Nanoparticles of Co were used as catalysts in the conversion of spent tea to biochemical (Mahmood and Hussain, 2010). It is claimed that in this pyrolysis process, Co nanoparticles reduce reaction temperature by up to 650°C. The liquid products yield of the reaction at 300°C and atmospheric pressure was about 60%.

Hydrothermal conversions of cellulose in the presence of two metal oxides (SnO₂ and ZnO) have been studied (Sinag et al., 2011). It has been found that using bulk ZnO as the catalyst increased the amount of glycolic acid by five times compared to when bulk SnO₂ was used in the hydrothermal conversion of cellulose at 300°C. Interestingly, when nano sized particles of these catalysts were used, the produced glycolic acid with ZnO catalyst was 12 times higher than that of nano-SnO₂. This result illustrates the excellent catalytic properties of the nanosized catalyst. The production of biogasoline and organic liquid products (OLP) were also studied in a fixed bed reactor with nanocrystalline zeolite as the catalyst and waste cooking palm oil as the biofeed (Taufiqurrahmi et al., 2011). Results showed that under different operating conditions, the conversion of 87.5-92.9 wt% of the feed is attainable. In such a condition, a gasoline fraction yield of 33.61- 37.05 wt% and an OLP fraction yield of 46.1-53.4wt% can be obtained. For zeolite Y with pore sizes of 0.67 nm as the catalyst, the optimum conditions of 458°C and an oil: catalyst ratio of 6 have been reported. The NiW-nano-hydroxyapatite (NiW-nHA) composite was used as the catalyst in hydrocracking of Jatropha oil. In the operating conditions of 360°C and 3 MPa about 92% of the feed was converted. The yield of C₁₅-C₁₈ alkanes in the product was up to 83.5wt%. By increasing operating temperatures it is possible to obtain 100% conversion of Jatropha oil in this process (Zhou et al., 2012).

3.2.1. Nanocatalysts for biodiesel production

In the biodiesel production method, transesterification is the chemical reaction between triglycerides and alcohol within the presence of a catalyst for producing monoesters. The triglyceride molecules are transformed to monoesters and glycerol. The transesterification method incorporates a sequence of three reversible reactions. The conversions of triglycerides to diglycerides, diglycerides to monoglycerides and glycerides into glycerol yield one ester molecule in each stage. The general transesterification reaction can be represented by Figure 2 (Gerpen, 2005).

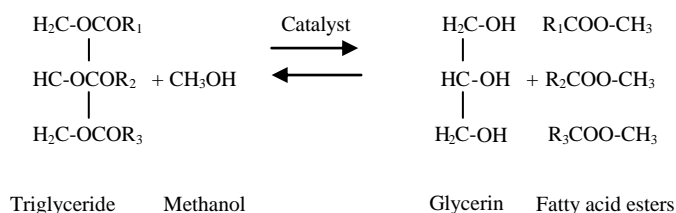


Fig.2. Transesterification of triglycerides with methanol.

The transesterification reaction of oil and alcohol with a homogeneous catalyst is the general method for the preparation of biodiesel. However, the homogeneous catalysts have many shortcomings, such as requiring large amounts of water, difficulties in product isolation, and environmental pollution caused by the liquid wastes. The use of "a green" method based on

heterogeneous catalysts is a new trend in the preparation of biodiesel. Biodiesel synthesis using solid catalysts instead of homogeneous ones could potentially lead to cheaper production costs by enabling reuse of the catalyst and opportunities to operate in a fixed bed continuous process. Heterogeneous catalytic methods are usually mass transfer resistant, time consuming and inefficient. Despite the solid phase, catalytic methods are intensively studied, the industrial applications are limited. This fact suggests that further research is necessary to solve current problems (Narasimharao et al. 2007). Nanocatalysts that have high specific surface and high catalysis activities may solve the above problems. A number of researchers have studied the preparation of nanosized heterogeneous catalysts to increase the catalytic activity. It is evident that the large surface area, which is characteristic of nanosized material, resulted in a rise within the amount of the catalytically basic and acidic sites. The nanocatalysts used for biomass to biodiesel conversion have been presented in Table 3.

Feyzi et al. (2013) used the magnetic Cs/Al/Fe₃O₄ as a nanocatalyst for transesterification reaction of sunflower oil, the optimal catalyst showed high catalytic activity for biodiesel production and the biodiesel yield reached 94.8%. For the transesterification of Pongamia oil with methanol, Obadiah et al. (2012), used calcined Mg-Al hydrotalcite as a solid base catalyst. The reaction conditions of the system were optimized to maximize the methyl esters conversion (about 90.8%).

Mguni et al. (2012) studied the transesterification of sunflower oil with nano-MgO precipitated and deposited on TiO₂ support as catalyst. Conversions of 84, 91 and 95% were measured at 225°C compared to 15, 35 and 42% at 150°C respectively for 10, 20 and 30wt. %MgO catalyst. Verziu et al. (2007) obtained biodiesel from rapeseed oil and sunflower oil using different nanocrystalline MgO catalysts in nanosheets form, which were prepared by conventional and aerogel method. Working under microwave conditions with these systems led to higher conversions and selectivity when preparing methyl esters, as compared to autoclave or ultrasound conditions. MgO can be used effectively as a heterogeneous catalyst for biodiesel transesterification. The exposed facet of the MgO has an important influence on activity and selectivity. A new nanocatalyst with potassium bitartrate as an active component on zirconia support was synthesized by Qiu et al. (2011). The transesterification reaction of soybean oil and methanol was catalyzed heterogeneously. The highest biodiesel yield of about 98.03% was obtained at methanol to oil molar ratio of 16:1, reaction time of 2 hr, a reaction temperature of 60°C and a catalyst amount of 6.0 wt%.

Lithium ion impregnated calcium oxide as a nanocatalyst for the biodiesel production from karanja and jatropha oils was studied by Kaur and Ali (2011). They reached a yield of 99% by using Li-CaO nanocatalyst for karanja oil transesterification after 1hr and jatropha oil after 2 hr.

Chang et al. (2010), reported preparation of CaO / Fe₃O₄ the nanometer magnetic solid base catalyst for production of biodiesel. They found that the conversion yield of transesterification reaction catalyzed by Ca (OH)₂ (Ca⁺²: Fe₃O₄=7) can reach 95% in 80 min, and the conversion of 99% obtained after 4 hr. Nanometer magnetic base solid catalyst was proposed as an efficient catalyst for biodiesel production because of its easy separation which led to a reduction in operating costs. Wen et al. (2010) reported the preparation of KF/CaO solid basic nanocatalyst for Chinese tallow seed oil. Optimal conditions for obtaining a 96.8% yield was a 12:1 molar ratio of alcohol to oil, 4wt. % of catalyst, reaction temperature of 65°C and reaction time of 2.5 hr. Deng et al. (2011) observed that hydrotalcite-derived particles with Mg/Al molar ratio of 3:1 could be an effective method for the production of biodiesel from Jatropha oil with a 95.2% yield after 1.5 hrs at ultrasonic conditions. Reddy et al. (2006) achieved a 99% biodiesel yield from soybean oil in room temperature by using nanocrystalline calcium oxides as a catalyst. They studied various forms of nano-CaO such as powder, pellets, and granules. They found that high yields of transesterification of soybeans oil are due to the higher surface area associated with small crystallite size and defects. Wang and Yang (2007) investigated nano magnesium oxides as a heterogeneous catalyst and its effect on biodiesel synthesis from soybeans oil. Nano-MgO showed higher catalytic activity in supercritical/ subcritical temperatures. It was evidently superior to that of non-catalysts. The apparent

Table 3
Nanocatalysts used for biodiesel production along with their operating conditions.

No.	Nano Catalyst	Size (nm)	Feedstock	Operation Condition				Biodiesel yield (%)	Ref.
				Temp. (°C)	Alcohol:oil ratio	Catalyst loading (wt. %)	Reaction Time (min)		
1	Cs/Al/Fe ₃ O ₄	30-35	Sunflower oil	58	14:1	4	120	94.80	(Feyzi et al. 2013)
2	Hydrotalcite (Mg-Al)	4.66-21.1	Pongamia oil	65	6:1	1.5	240	90.8	(Obadiah et al. 2012)
3	MgO Supported on Titania	-	Soybean oil	150-225	18:1	0.1-7	60	95	(Mguni et al. 2012)
4	MgO	50-200	Sunflower oil Rapeseed oil	70-310	4:1	-	40 -120	98	(Verziu et al. 2007)
5	ZrO ₂ loaded with C ₄ H ₄ O ₆ HK	10-40	Soybean oil	60	16:1	6	120	98.03	(Qiu et al. 2011)
6	Lithium impregnated calcium oxide (Li-Cao)	40	Karanja oil Jatropha oil	65	12:1	5	60 120	99	(Kaur and Ali 2011)
7	Magnetic solid base catalysts CaO / Fe ₃ O ₄	49	Jatropha oil	70	15:1	2	80	95	(Chang et al. 2010)
8	KF/CaO	30-100	Chinese tallow seed oil	65	12:1	4	150	96	(Wen et al. 2010)
9	Hydrotalcite-derived particles with Mg/Al molar ratio of 3:1	7.3	Jatropha oil	45	4:1	1	90	95.2	(Deng et al. 2011)
10	Cao	20	Soybean oil	23-25	27:1	-	720	99	(Reddy et al. 2006)
11	Mgo	60	Soybean oil	200- 260	6:1	0.5-3	12	99.04	(Wangand Yang 2007)
12	KF/CaO-Fe ₃ O ₄	50	Stillingia oil	65	36:1	4	180	95	(Hu et al. (2011)
13	TiO ₂ -ZnO ZnO	34.2 28.4	Palm oil	60	12:1	-	300	92.2 83.2	(Madhuvilakku and Piraman, 2013)
14	KF/ Al ₂ O ₃	50	Canola oil	65	6:1	3	480	97.7	(Boz et al. 2009)
15	ZnO nanorods	-	Olive oil	150	15:1	1	480	94.8	(Molina 2012)
16	CaO/MgO	-	Jatropha oil	64.5	18:1	2	210	92	(Chang et al. 2010)
17	Ca (OH) ₂ -Fe ₃ O ₄ (Ca ²⁺ : Fe ₃ O ₄ =7)	-	Jatropha oil	70	15:1	2	240	99	(Chang et al. 2010)

activation energy with nano-MgO was lower than that without MgO. They found that Nano-MgO can catalyze the transesterification reactions, but its catalytic ability was quite weak under normal temperature. At a temperature of 60°C, the methyl ester yield was only about 3% in 3 hr when 3 wt. % of nano- MgO was added. Thus, it is desirable to find a more efficient method for transesterification of triglycerides by using methanol with a higher

reaction rate under more moderate temperature and pressure. observed with a 99.04% yield in 12 min. Hu et al. (2011) investigated nano-magnetic solid base catalyst KF/CaO-Fe₃O₄ for transesterification of stillingia oil, extracted from the seeds of Chinese tallow (*Sapium sebiferum*). The best activity obtained with nano-magnetic solid base catalysts with 25 wt. % KF loading and 5 wt. % Fe₃O₄, calcined at 600°C for 3 hr.

Madhuvilakku and Piraman(2013) used both ZnO and TiO₂-ZnO nanocatalysts for production of biodiesel from palm oil. The substitution of Ti ions on the Zinc lattice led to the creation of defects, responsible for stable catalytic activity. A 92.2% yield was attained with 5 hr. at lower catalyst loading of 200 mg of TiO₂-ZnO nanocatalyst at 6:1 methanol to oil molar ratio and 60°C. The TiO₂-ZnO mixed oxide nanocatalysts illustrated a significantly improved performance which could be a potential catalyst in the large-scale biodiesel production compared to the ZnO nanocatalyst.

Boz et al. (2009) reported that the optimum loading amount of KF on nano- γ -Al₂O₃ was 15 wt. %. The conversion of triglycerides to biodiesel reached values which were as high as 97.7 ± 2.14%. Such high biodiesel yields reflect the benefits of reaching relatively high basicity and the use of nanosized catalyst particles for Canola oil transesterification. Molina (2012) studied on ZnO nanorods as catalyst for biodiesel production from olive oil. The catalytic performance of the ZnO nanorods was slightly better than that of the conventional ZnO. The reported yield of Olive oil to biodiesel was 94.8 % by using ZnO nanorods compared to 91.4% by commercial ZnO.

Based on different studies on nanocatalyst application for biodiesel production, it is evident that the large porous catalytic surface increased the contact between alcohol and oil, leading to an increase in nanocatalytic effectiveness. Utilization of different edible and nonedible oils for transesterification reactions by using both acid and alkali nanocatalysts show the important influence of these catalysts regarding activity and selectivity. The presented results reveal that the high specific surface area of nanostructure materials in comparison with bulk catalysts is favorable for contact between catalyst and substrates, which effectively improve the yield of products.

4. Conclusion

Without doubt, it is necessary to replace fossil energy resources with new safe sources. Among the existing choices, biomass seems to be the best option. The energy released from biomass is renewable and environmentally friendly, so it is strongly recommended to be applied. It is obvious that many methods are available for converting biomass to biofuel. However, some of the key challenges in biomass conversion provide new research potential for improving quality of products and solving its related environmental problems. Introducing nanotechnology research to biomass conversion has witnessed rapid growth, which is mainly related to unique property of possessing high specific surface area. In this paper a review of thermochemical nanocatalytic processes as a major technology for biomass conversion has been provided. Thermochemical biomass gasification converts biomass to a combustible gas mixture through partial oxidation at relatively high temperatures. The products mainly include carbon monoxide and hydrogen (syngas). In biomass gasification the nanocatalysts which have mostly been used to reduce tar formation are NiO, CeO₂, ZnO, SnO₂. Moreover, the application of nanoalloys such as (CeZr) xO₂ and Ni₃Cu (SiO₂)₆ provide higher performances at relatively lower gasification temperatures. In biomass liquefaction nanocatalysts have been successfully used to increase the liquids yields and also enhance the value-added products. The higher temperature in the liquefaction process increases gaseous products. Nanocatalysts successfully reduce reaction temperatures causing an increase in the liquids products which means an improvement in the liquefaction operation. In pyrolysis of spent tea Co nanoparticles reduce the operating temperature to 300°C and increase the liquid product yield to 60%. Use of ZnO and SnO₂ nanoparticles in hydrothermal conversion of cellulose shows better liquid product yield in comparison with using these catalysts in bulk dimension. Nanocrystalline zeolite was used in catalytic conversion of cooking palm oil which has attained about 93% conversion at optimum temperature of 458°C. The nanocomposite catalyst of NiW-hydroxyapatite may convert 100% of Jatropha oil in catalytic the hydrocracking process. Nanocatalysts for biodiesel production significantly improve the yield of products. The main nanometal oxides that have been used for biodiesel production are Zn, Ca, Mg, Zr. These have either been used individually or supported on different materials. However some other catalysts such as Li, Cs, KF have been utilized for edible and nonedible feedstock. In addition, magnetic nanoparticles functionalized with different catalysts have been implied in biodiesel production, facilitate the catalyst recovery. The results of using KF/CaO and nanomagnetic KF/CaO-Fe₃O₄ catalysts for biodiesel preparation show better performance of KF/CaO catalyst with a higher surface area of about 109 m²g⁻¹

at the same operating conditions compared to KF/CaO-Fe₃O₄ catalyst with a surface area of 20.8 m²g⁻¹. Loading KF on nano Al₂O₃ support could obtain a higher yield of about 97.7% compared to 96.8% for KF/CaO catalyst. But it must be noted that the operating conditions of using KF/ Al₂O₃ catalyst were relatively higher than that of KF/CaO catalyst. The alcohol: oil ratio, catalyst loading and reaction time were 15:1, 3 wt. % and 480min in comparison with 12:1, 4wt. % and 150min respectively for KF/ Al₂O₃ and KF/CaO catalysts. Despite using different feedstocks, the better performance of KF/CaO catalyst may be related to its higher surface area (109 m²g⁻¹) compared to the value of 41.7 m²g⁻¹ for KF/ Al₂O₃ catalyst. The highest biodiesel yield was obtained using nanocatalysts Li-CaO and CaO at reaction time of 120 and 720min, temperature of 65 and 25°C and methanol to oil molar ratio of 12 and 27, respectively. Similar yield has been obtained using a nano-MgO catalyst but at a higher temperature of about 200-260°C. In general to achieve high performances at relatively mild operating conditions, it is necessary to increase the reaction time while at ordinary reaction times, it is necessary to apply severe operating conditions. Comparing the results of using different supported and unsupported MgO catalysts revealed that decreasing the reaction time led to an increase in reaction temperatures for achieving higher performances. As a whole using milder operating conditions led to a reduction in energy consumption requirements of the process which could be feasible with using nanocatalysts.

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