



## Nano catalysts in effective biomass processing

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### ABSTRACT

The population of the world is increasing day by day very rapidly and the development in industrial field raise the demand of energy. Due to limited resource of non-renewal energy resource, hike in crude oil prices and ever increasing pollution, human civilization has been forced to look for renewal energy recourses and hence biomass has got a great attention in this regard. Currently biomass is supplying about 10-15% energy of the world and it is expected to contribute half of the energy of the whole world by the year 2050. Biomass is generally processed by gasification and direct liquefaction to produce gases and liquids used as energy, but it also has to face the problems caused by heterogeneous catalyst, in the form of increase in material cost, decrease of catalyst performance over the time, the relative difficulty in reclaiming and recycling, sulfur poisoning and deactivation. Nano technology has shown a promising hope in this regard. Gasification provides a route in converting the highly distributed and low value lignocellulosic biomass to hydrogen rich gas, namely the synthetic gas, as well as hydrogen gas. Moreover, the resulting gas achieves a Fischer-Tropsch reactor favourable H<sub>2</sub>: CO ratio of about 9:1. The application of nanocatalysts improves yield at relatively milder operating conditions compared to bulk catalyst. Moreover nano catalysts are economically feasible on large scale with respect to heterogeneous catalyst. Also, the nano catalysts NiO, CeO<sub>2</sub>, ZnO, and SnO<sub>2</sub> are used to reduce tar formation during gasification. The nano catalyst treatment increases gas yield and, in one embodiment, cracks and gasifies lignin, which is generally inert in conventional gasification. The nanoalloy catalysts like CeZr, xO<sub>2</sub> and Ni<sub>3</sub>Cu (SiO<sub>2</sub>)<sub>6</sub> achieve the increased conversion efficiency and cracking of any biomass at relatively lower gasification temperature. As such combination of catalyst and methods invented till now, provides a means to increase gas yields while lowering the lignin content in the resulting product relative to conventional gasification.

**KEY WORDS:** Biomass, Catalyst, Gasification, Liquefaction, Lignin, Non-Renewal energy resource, Nano alloy.

### 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 fore casted by the International Energy Agency that the global peak in oil production will be between 1996 and 2035.<sup>[1]</sup> 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. The primary alternative sources of energy systems that can replace fossil fuels are water, wind, solar energy, and biomass.<sup>[2]</sup> 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 CO<sub>2</sub> is emitted from the burning of fossil fuels, and this is predicted to increase about 60% by 2030.<sup>[3]</sup> Therefore, using bio derived fuels is crucial to reducing the carbon footprint. 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, non edible 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.<sup>[4]</sup> The photosynthesis yield of approximately 720 billion tons per year, make the largest organic raw material cellulose resource in the world. In general all kinds of biomass can be used as feedstock including starchy, triglyceride and lignocellulosic feedstock. Biomass can be converted to bio fuels and bio power 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.<sup>[5]</sup> 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. 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.<sup>[6,7]</sup> 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.

## **BIOMASS**

Biomass is biological material derived from living or recently living organism. It most often refers to the plants or plant based materials which are significantly called lignocellulosic biomass.<sup>[8]</sup>

## **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.<sup>[9]</sup> 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.<sup>[10,11]</sup> In the following section gasification and direct liquefaction processes have been described as two main thermochemical conversion methods.

## **GASIFICATION**

Gasification is a process that converts organic or fossil fuel based carbonaceous material into CO, H<sub>2</sub>& CO<sub>2</sub>. This is achieved by reacting the material at high temperature (>7000C),<sup>[12]</sup> without combustion, with a controlled amount of oxygen and/or steam.

## **LIQUEFACTION**

Two main routes can be considered industrially for the liquefaction of biomass to bio-oils and these include hydrothermal liquefaction, and catalytic liquefaction. Hydrothermal liquefaction is based on the superior properties of water at higher temperatures and pressures.<sup>[13]</sup> 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 sever.<sup>[14]</sup> As a result, hemicellulose and cellulose are hydrolyzed very quickly at these conditions. Hydrothermal liquefaction has another important advantage.

## PYROLYSIS

Pyrolysis is a thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen (or hydrogen).<sup>[15]</sup> It involves the simultaneous change of chemical composition and physical phase, and is irreversible in nature.<sup>[16]</sup>

## CATALYST SYSTEM USED

Generally alkali metal salt of weak acids like K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>S and Na<sub>2</sub>S can be used to catalyze steam gasification of coal. 10-20% by weight<sup>[17]</sup> K<sub>2</sub>CO<sub>3</sub> could lower acceptable bituminous coal gasifier temperature from 9250C to 7000C.<sup>[18]</sup>

## DISADVANTAGES OF USING HETEROGENEOUS CATALYST SYSTEM

- Use of above type of heterogeneous catalyst system increase the material cost.
- Such catalyst losses its activity over a period of time.
- There is another disadvantage as a difficulty in recycling and reclaiming the catalyst in the biomass processing.<sup>[19]</sup>
- Catalyst suffers by poisoning in such systems used in the process.
- Many catalysts are sensitive to particular chemical species which bond with the catalyst or after it such a way that it no longer functions. Eg:- sulfur poison several types of catalyst including nickel, iron, palladium and platinum.<sup>[20,21]</sup>

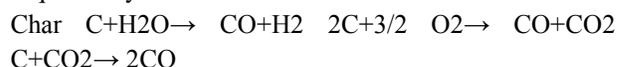
## APPLICATION OF NANOCATALYSTS IN BIOFUEL PRODUCTION

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).<sup>[22]</sup> 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. Two main approaches employed for controlling the production of tar are, including treatments inside the gasifier (primary methods)<sup>[23]</sup> and hot gas cleaning after the gasifier (secondary methods).<sup>[24]</sup> 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. 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.<sup>[25,26,27]</sup> 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. 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. Char formation during the pyrolysis step of gasification can be expressed by the following equation:<sup>[28]</sup>

Biomass → Volatiles + char

Depends on using steam, oxygen or CO<sub>2</sub> as gasification agent, conversion of the residual chars can be presented sequentially as follows:



Potassium, sodium and calcium have been found to be the most effective catalysts for promoting char gasification in steam or carbon dioxide media.<sup>[29]</sup> 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. Catalytic tar cleaning is potentially attractive because no additional input energy is necessary. The important reactions during tar reduction include steam reforming,<sup>[30]</sup> dry reforming, thermal cracking, hydrocracking,<sup>[31]</sup> hydro reforming and WGS reactions.

## 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, CeO<sub>2</sub>, ZnO, and SnO<sub>2</sub>. Moreover, the application of nanoalloys such as (CeZr) xO<sub>2</sub> and Ni<sub>3</sub>Cu (SiO<sub>2</sub>)<sub>6</sub> 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 SnO<sub>2</sub> 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, and 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-Fe<sub>3</sub>O<sub>4</sub> catalysts for biodiesel preparation show better performance of KF/CaO catalyst with a higher surface area of about 109 m<sup>2</sup>g<sup>-1</sup> at the same operating conditions compared to KF/CaO-Fe<sub>3</sub>O<sub>4</sub> catalyst with a surface area of 20.8 m<sup>2</sup>g<sup>-1</sup>. Loading KF on nano Al<sub>2</sub>O<sub>3</sub> 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/ Al<sub>2</sub>O<sub>3</sub> 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/ Al<sub>2</sub>O<sub>3</sub> and KF/CaO catalysts. Despite using different feedstocks, the better performance of KF/CaO catalyst may be related to its higher surface area (109 m<sup>2</sup>g<sup>-1</sup>) compared to the value of 41.7 m<sup>2</sup>g<sup>-1</sup> for KF/ Al<sub>2</sub>O<sub>3</sub> 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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