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Enhancing Combustion Efficiency Using Nano Nickel Oxide Catalyst in Biomass Gasifier

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Abstract

The objective of this work is to develop novel supported Nano Nickel Oxide [Nano-NiO] catalyst. For tar removal in biomass gasification / phyrolysis significantly enhance the quality of the produced gas. The experiments demonstrated that the tar yield after addition of the catalyst was reduced significantly. The tar removal efficiency reached to 99% for catalytic phrolysis at 700^{o}c and the gas yield after addition of the catalyst increased markedly. The composition of gas products before and after addition of the catalyst in the process also changed significantly. The percentages of CO2, In the product gas after addition of the Nano-NIO catalyst were obviously reduced, while those the valuable H2 and CO strongly increased. Therefore using the Nano -NiO catalyst in biomass gasification/phrolysis can significantly improve the quality of the produced gas.

***Index Terms* — Nano Nickel Oxide, Biomass gasification, Phyrolysis**

I. Introduction

Biomass is decomposed in thermo-chemical processes having various combinations of temperatures and pressures. Gasification is a process in which combustible materials are partially oxidized. The product of gasification is a combustible synthesis gas. Since gasification involves the partial oxidization of the feed rather than complete, gasification processes operate in an oxygen-lean environment. Gasification of Biomass is carried out by one of the following two processes. Heating the biomass with limited air or oxygen and heating at high temperature and high pressure in presence of steam and oxygen. Biomass can be converted into gases, liquids, and solids through pyrolysis at temperatures of 500 - 900°C by heating in a closed vessel in the absence of oxygen.

II. Thermal Properties of Biomass

Each type of biomass has its specific properties which determine its performance as a fuel in

combustion. Most important properties regarding thermal conversion of fuels is as follows:
Moisture content, Ash content, volatile matter content, Elemental composition and Calorific value

III. Calorific Value

The calorific value is one of the most important characteristics of a fuel, and it is useful for planning and control of the combustion plants. It indicates the amount of heat that develops from the mass (weight) in its complete combustion with oxygen in a calorimeter standardize. It is defined as the amount heat energy released during the complete combustion of unit mass of biomass.
There are two types of calorific value (usually expressed in kcal/kg or MJ/kg) might be considered:

1. Higher heating value (HHV): it is the amount of heat released by a complete combustion of a mass unit of a sample at constant volume in an oxygen atmosphere and at the standard conditions (101.3 kPa, 25°C). The HHV takes into account the latent heat of vaporization of water, and it assumes that the water component is in liquid state at the end of combustion.
2. Lower heating value (LHV), doesn’t include the water condensation heat. The high heating value can be determined experimentally in the laboratory with adiabatic calorie.

IV. 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 non condensable 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(4). The slow pyrolysis can disport to conventional charcoal production and intermediate pyrolysis. 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 (5).

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 %(6).

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 approximately500°C. More than 70% of pyrolysis products are condensed to liquid due to their fast heating and vapour condensation of less than two seconds(7). The pyrolysis condensates show some hydrophilic behaviour caused by their high oxygen content, up to 45%. This behaviour 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 deoxygenating of hot stream of biomass pyrolysis products (8).

In a research work 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 macro algae powder has been converted to bio-oil by fast pyrolysis method in a free fall reactor. Macro algae (Enteromorphaprolifera) have 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.

V. Tar removal

The effect of reforming temperature on tar removal and syngas composition were investigated for the temperature range of 650°C to 850°C while the Ni loading and gas residence time were fixed at 15wt% and 0.3 s, respectively. As shown in Fig.2a, tar removal rate increased with increasing reaction temperature in all cases. Under the same reaction conditions, nano-Ni/char catalyst showed the highest tar removal rate at all temperatures, ranging from 91% to 99%(13).

The Ni/char catalyst also achieved higher than 90% tar removal rates, even at relatively low temperatures (<800°C) where the Ni/γ-Al2O3was not very effective. However, when temperatures were at 800°C or higher, Ni/γ-Al2O3was as effective as nano-Ni/char and better than Ni/char in tar removal. It indicates that the Ni/γ-Al2O3 catalyst requires higher reaction temperature, while Ni/char and nano-Ni/char can work effectively at lower temperatures.

If 95% tar removal is the target, a reaction temperature of 750°C is needed for nano-Ni/char, and a minimum of 800°C is required for the other two catalysts. The higher catalytic performance of Nano-Ni/char and Ni/char at a relatively low temperature could be explained by the fact that char itself decomposes heavy tars into small hydrocarbons at low temperatures(Gilbert et al., 2009), but γ-Al2O3lacks of the ability. It is also well known that nickel catalysts have low catalytic activity when reaction temperature is under 750°C.

The effect of Ni loading on tar removal and syngas reforming was studied with Ni/char, nano Ni/char and Ni/γ-Al2O3catalysts at 0.3 s gas residence time and 800°C reaction temperature. As shown in Fig. 2b, tar removal rate of all catalysts steadily but slightly increased when Ni loading increased from 5% to 15%.

The nano-Ni/char catalyst showed better performance than Ni/char and Ni/γ-Al2O3catalyst when Ni loading was in the range of 5 to 15 wt.% probably due to better adhesion and more uniform distribution of NiO particle on char particles. However, the performance of nano-Ni/char decreased when nickel loading further increased up to 20 wt %. This is due to nickel dispersion rate decreased significantly with increasing nickel loading(Bartholomew and Boudart, 1976). It can also be seen that Ni/γ-Al2O3with 5 wt% Ni loading for tar removal is significantly lower than Ni/char and nano-Ni/char.

This could be attributed to the different ways the catalysts were prepared. In γ-Al2O3 supported catalysts, NiO is also formed inside the support via the impregnating and calcining methods. NiO inside of the support is not as active as on the surface causing loss of active nickel. On the other hand, all NiO particles stay on the surface of chars in the mechanical mixing processing, leading to more efficient use of nickel (14).
Nickel Oxide (NiO) Nano powder / Nanoparticle (NiO, 99%, 10-20 nm)

VI. Nickel Oxide Nano particle Features

Nickel oxide nano powder is green black, 20nm, spherical, with purity of 99.5% and density of 6.827 g/cm3. It has a wide range of uses.

Table 1 NIO properties

Item	Appearance	APS	Purity	SSA	Morphology
Nickel Oxide Nano particle	Grey Dark	20nm	99.99%	50m2/g	Nearly Spherical

VII. Nickel Oxide Nanoparticle Application

1. Catalyst
2. Adhesive and coloring agents for enamel;

3. Active optical filters;
4. Antiferromagnetic layers;
5. Automotive rear-view mirrors with adjustable reflectance;
6. Cathode materials for alkaline batteries;
7. Electro chromic materials;
8. Energy efficient smart windows (with adjustable absorption and reflectance in the visible and near-IR wavelength range) P-type transparent conductive films;
9. Pigments for ceramics and glasses;
10. Materials for gas or temperature sensors, such as formaldehyde sensor, CO sensor, H2 sensor
11. Counter electrode

VIII. Nickel Oxide (NiO) Nano particles – Properties

Chemical Properties

The chemical properties of nickel oxide nano particles are outlined in the following table.

Table 2 NIO chemical date and composition

Chemical Data		Chemical Composition	
Chemical symbol	NiO	**Element**	**Content (%)**
CAS No.	1313-99-1		
Group	Nickel 4 Oxygen 16	Nickel	78.55
Electronic configuration	Nickel [Ar]3d8 4s2 Oxygen [He] 2s2 2p4	Oxygen	21.40

Physical Properties

The physical properties of nickel oxide nano particles are given in the following table.

Table 3 NIO physical properties

Properties	Metric	Imperial
Density	6.67 g/cm3	0.240 lb/in3
Molar mass	74.71 g/mol	-

IX. Nano catalysts 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. 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. 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. 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.

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 Dolomit. 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. .

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. 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 (nona NiO, 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.

X. Experimental Biomass gasifire operating conditions

Table 4 Operating conditions

Parameter	Condition
Temperature	800 degree Celsius
Biomass feed rate	1kg/h
Air	1000 I /h
Wood Sand	1kg
Nano- NiO catalyst	60g

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COMPONENT	READINGS	
H2S	00.01	%
CARBON DIOXIDE CO2	04.00	%
METHANE CH4	90.69	%
O2	00.81	°F
	0.04	%
TEMP	850	°C

Figure 1 Gas Analyzer

XI. Formula

Higher (or) Gross Caloric Value [H.C.V]
Delong's formula

$$H.C.V = 9270S + 33800C + 144000 [H_2 - O_2/8] kj/kg$$

Lower (or) Net Calorific value [L.C.V]

$$L.C.V = H.C.V - [9H_2 * 2465] kj/kg$$

Indirect Determination method for combustion efficiency

$$\eta_c = 100 - L_{thermal} - L_{chemical} \; \%$$

Where,

η_c = Combustion efficiency [%]

$L_{thermal}$ = Thermal losses by sensible heat of flue gas [%]

$L_{chemical}$ = Chemical losses by incomplete combustion [%]

$$L_{thermal} = \frac{(T_{fg} - T_A)\{ 1. 39 + 122/CO_2 + CO + 0.02u \}}{NCV_{Dryfuel}/100\text{-}0.2442u} \quad [\%]$$

$$L_{chemical} = \frac{CO * 11800}{(CO_2+CO) * (NCV_{Dry\ fuel}/100) - (0.2442\ u)} \quad [\%]$$

Where,

T_{Fg} = Fuel gas temperature [°C]
T_A = Ambient temperature [[°C]
O_2 = Oxygen concentration in dry flue gas [vol.-%]
CO_2 = Carbon dioxide concentration in dry flue gas [vol.-%]
CO = Carbon monoxide concentration in dry flue gas [vol.-%]
$NCV_{Dry\ fuel}$ = Net calorific value of absolutely dry fuel [kj/kg]
U = Humidity of fuel [Wt%]

XII. Implementation and results

Table 5 Product of the gas before add Nano NiO Catalyst

S. NO.	C	CO	CO2	CH4	Cn Hm	H2	O2	Net c. v. Kj/kg	ηc (%)	T° (C)
1	37.5	4.41	6.72	0.58	0.05	2.65	8.62	14351.49	29.42	450°C
2	39.60	4.73	7.02	1.34	00.21	3.08	12.73	14845.302	30.94	497°C
3	42.10	5.19	8.33	1.69	00.19	2.21	6.28	15790.7115	36.2	543°C
4	44.33	6.62	9.3	1.33	00.40	2.65	7.66	16843.63	39.2	600°C
5	49.70	8.01	9.82	1.89	0039	2.69	11.08	18081.0235	40.6	659°C

Table 6 Product of the gas after add Nano NiO Catalyst

S. NO.	C	CO	CO2	CH4	Cn Hm	H2	O2	Net c. v. Kj/kg	ηc (%)	T° (C)
1	45.18	4.69	5.19	2.60	0.21	6.40	7.66	21627.36	45.08	450°C
2	49.73	4.93	6.72	2.07	0.20	6.45	8.62	23114.2075	53	497°C
3	53.64	6.30	7.51	2.82	0.19	7.26	10.93	25128.369	56.8	543°C
4	57.13	7.28	10.56	2.20	0.23	7.59	11.23	26524	62.43	600°C
5	60.00	8.01	9.82	3.26	0.24	11.23	12.73	28184.52	63.11	659°C

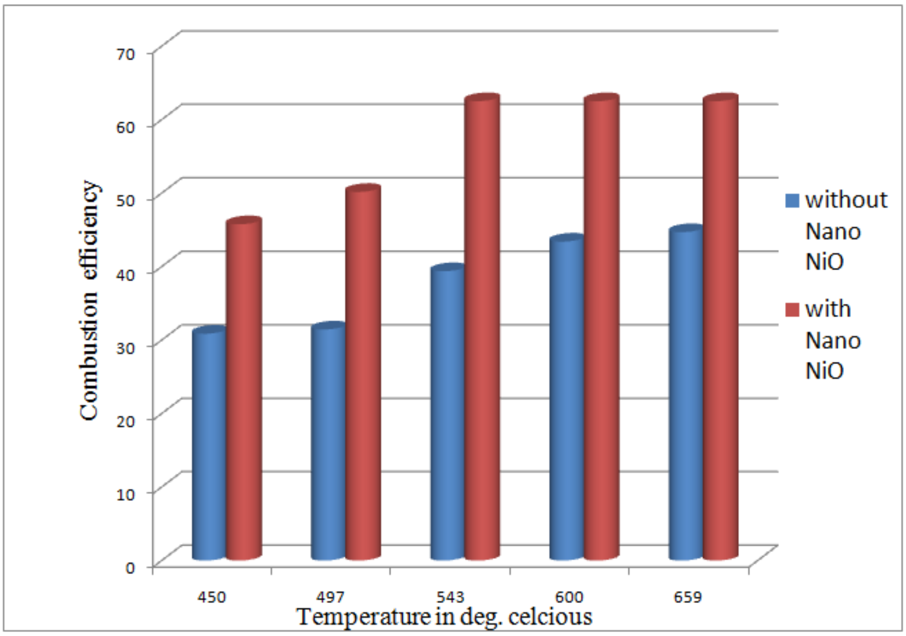

Figure 2 Combustion efficiency with and without NiO

Without doubt it is necessary to replace fossil energy resources with new safe source. Among the existing choices, biomass seems to be best option. The energy released from biomass is renewable and environmental friendly, so it is strongly recommended to be applied. The catalyst especially in eliminations of tar, the quality of the product gas of biomass gasification is improved.

XIII. Conclusion

The results of Nickel Oxide [NiO] catalytic reactions indicate that tar was favourably converted to synthesis gas [H2, CO2, CH4 & CO] at high temperature. Nano-nickel oxide is very effective in tar removing and adjusting CO-H_2 ratio. The nano-nickel oxide support and provide higher resistance to coke formation. Coke deposition on catalyst results in deactivation of the primary concern in catalytic biomass gasification and pyrolysis. Carbon deposition can be reduced addition of nano-nickel oxide. Synthesis gas production Nano - Nickel Oxide [Nano -NiO] catalyst has good stability and suitability in enhance the combustion efficiency.

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