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Full Length Research Paper

New nanomaterial and process for the production of biofuel from metal hyper accumulator water hyacinth

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Three different studies were performed for the conversion of water hyacinth (*Eichhornia crassipes*) plant into biofuel. In the first study, water hyacinth was saccharified with diluted sulfuric acid (1% v/v at 110°C for one hour), fermented by yeast (*Saccharomyces cerevisiae*). The results showed the formation of 55.20% ethanol and 41.66% acetic acid. In another experiment, water hyacinth was gasified by using Ni and Co nano catalysts at 50 - 400°C and atmospheric pressure. In catalytic gasification, CH_4 (2.41 - 6.67%), C_2H_4 (19.74 - 45.52%), C_3H_4 (21.04 - 45.52%), CH_3OH (1.43 - 24.67%), and C_3H_8 / CH_3CHO (0.33 - 26.09%) products were obtained. In this study, anatase form of titanium dioxide photocatalyst was used. The reaction was performed at room temperature which gives methane, methanol and ethanol. This study also reports an interesting finding that metal contaminated water hyacinth could be used for not only the production of biofuel but also hydrocarbons.

Key words: Water hyacinth, bioethanol, metal, cobalt nano particles, nickel nano particles, photocatalyst, biofuel, hydrocarbons.

INTRODUCTION

Water hyacinth, a native of South America, is also abundantly found in South Asia. Under favorable conditions, a growth rate as high as 17.5 metric tons of wet water hyacinth per hectare per day has been reported (Shoeb and Singh, 2000). Fresh plant contains 95.5% moisture, 0.04% N, 1.0% ash, 0.06% P_2O_5, 0.20% K_2O, and 3.5% organic matter. On a zero-moisture basis, it is 75.8% organic matter, 1.5% N and 24.2% ash. The ash contains proteins contain 0.72 g methionine, 4.72 g phenylalanine, 4.32 g threonine, 5.34 g lysine, 4.32 g isoleucine, 0.27 g valine and 7.2 g leucine (Matai and Bagchi, 1980). Gohl (1981) reported that 5.9 g dry matter of Indian hyacinth 28.7% K_2O, 1.8% Na_2O, 12.8% CaO, 21.0% Cl_2 and 7.0% P_2O_5. Nutritive values showed that its 100 g crude contains 13.1% of crude proteins, 18.2% crude fibres, 15.3% ash, 2.16% Ca and 0.41% P.

Heavy metals are ubiquitous environmental contaminants in industrialized countries. Such metallic pollution may be easily controlled by water hyacinth (Tiwari et al., 2007; Mishra and Tripathi, 2008). Developing cost effective and environment friendly technologies for the remediation of soils and wastewaters polluted with toxic substances is a topic of global interest. The value of metal-accumulating plants to wetland remediation has been recently realized (Prusty et al., 2007). The concentrations of metals in plants like water hyacinth can be measured by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometery) with an ultrasonic nebulizer. It shows maximum detection limits with less chance of errors (Liao and Chang, 2004). In order to use these high metal content

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Abbreviations: GC, Gas chromatography; **GC-MS,** gas chromatography coupled to mass spectrometry; **CID,** charge injection device; **IR,** infrared; **SEM,** scanning electron microscope; **TEM,** transmission electron microscope; **XRD,** X-ray diffraction; **HPLC,** high performance liquid chromatography; **FCC,** face-centred cubic; **PCA,** photocatalytic activity; **UV,** ultra-violet.

containing water hyacinth plants, we developed a new material and process to convert this as a source of alternate energy.

There have been many discussions regarding substitute materials to replace petroleum and other decreasing natural fuel resources. These can be derived from plants that is, biomass can be converted into hydrocarbons and biofuels (Ohno and Fukaya, 2009). It would be of course beneficial to obtain energy from inedible biomass like water hyacinth containing metallic pollutants. Water hyacinth contains large quantity of cellulose that can be converted into bioethanol by enzymes. The conversion of biomass into hydrocarbons like methane utilizes a complex but reasonably well understood biochemical route. Digestion of water hyacinth biomass into methane anaerobically under mild conditions of pressure and temperature is possible. Thermal gasification of biomass is possible at much higher temperatures (> 500°C) and takes advantage of an equally complex series of chemical reactions that occur between carbon-containing com-pounds, water and oxygen (Butner et al., 1988).

Biomass and waste-to-energy facility can also contribute to the country's economy by providing jobs apart from generating electricity. Recently, there has been considerable interest in developing cost effective and environment friendly technologies for fuel production (Mahmood et al., 2005). A computer based model was developed and was tested against various experimental data of glucose, pyrocatechol and cornstarch in supercritical water gasification process. This model predicts that high gas production can be achieved at 750°C temperature (Aye and Yamaguchi, 2006). Thermal decomposition of biomass with catalyst shows that primary gases like CO, CO_2, CH_4 and soot etc are formed and than on reforming other hydrocarbons (Davidian et al., 2006). All methods for production of fuels have their own drawbacks which include the use of high pressure/ temperature or both, long reaction times, low yields, toxic solvents and nonselective stoichiometric amounts of reagents, that may lead to formation of quantitative amounts of undesirable salts or require the use of a pyrophoric catalyst. However, there is strong need to develop new green catalyst that should be efficient, involve an easy work-up and afford greater yields in shorter reaction times. In this regard, Co has extensively been used for catalytic gasification. He et al. (2008) studied the influence of catalyst and temperature on yield and product composition during gasification. They used temperature range 750 - 950°C. However, reactions catalyzed by Co are very slow owing to low surface area of the catalyst. It was therefore worthwhile to develop a new green catalyst that could enhance the reaction rate. Work in the field of Co metal nano particles as catalyst in synthetic organic chemistry has gained much attention (Kidwai et al., 2006). Various scientists have examined the role of nano particles in catalysis under well-controlled environments (Valden et al., 1998). Gates (2000) and others have employed molecular nano particles in catalysis. The benefits of applying nanotechnology to catalysis include improved activity, lifetime resistance to poisoning and other novel abilities. The improvements and novelties cannot always be achieved with catalysts prepared by other methods. An example of expanding the catalytic capabilities of regular catalysts through nano scale manipulation is cobalt-based catalysis. Co nano particle catalyst may be influenced by their size, structure and by other additional components such as Si, Ni, and Mg. For example, Co or Co oxide nanostructures are known to be effective catalysts for oxidation/ reduction reactions (Yang et al., 2001; Kesavan et al., 2001; Son et al., 2002). Cobalt nano particles, in particular being cheap, need mild reaction conditions for high yield of product in short reaction time as compared to the traditional catalysts.

Nickel catalyst is also widely used in gasification (Davidian et al., 2006; Kimura et al., 2006 Svoboda et al., 2007; Swierczynski et al., 2007). The melting point of nano particles is size dependent. On mixing nano particles of Ni with Co, catalytic ability is increased (Guo et al., 1995).

Fermentation of water hyacinth by *Saccharomyces cerevisiae* can be used for ethanol production at (Masami et al., 2008). Water hyacinth can be converted into methane by using methanogenic, acidogenic bacteria, anaerobic condition, volatile organic compounds and animal waste (Kalle et al., 1985; Jayaweera et al., 2007).

Photocatalyst is also very useful in energy production from biomass. Stamate and Lazar (2007) reported that in the absence of a catalyst active substance, oxidation of most hydrocarbons proceeds slowly, which can be explained by kinetic arguments. A photocatalyst decreases the activation energy of a given reaction. In the result of photo-induced processes, particles with strong oxidation and reduction ability often occur. Titanium dioxide based anatase showed highest photocatalytic activity. For removal of phenol titanium dioxide, base photocatalyst was used by Suryaman et al. (2009). A wide range of organic compounds are converted into water and carbon dioxide. This behavior of photocatalyst is responsible for killing pathogenic microorganisms.

The goal of this study was to use metal polluted water hyacinth plants for production of fuel gases and alcohols at low temperature and at atmospheric pressure.

MATERIALS AND METHODS

Collections of samples for metal analysis, moisture content, dry weight, ash and crude fiber contents

Water hyacinth samples were collected washed and dried. Moisture content, dry weight, ash content and crude fiber content was calculated by the method described by Okoye et al. (2002). Dry plant samples were digested in HNO_3 and $HClO_4$ as reported by Rayon et al. (2001). The digested samples were analyzed by Thermo Jarrell Ash Inductively coupled plasma atomic spectrometer. The detector was charged using the following conditions: RF power was 1150 W, flush pump rate was 1000 rounds per minutes, CID (charge injection device), integration time (low) was 15 s, CID

integration time (high) was 5 s, argon flow rates were 0.51/min (auxiliary) and 30 psi (nebulizer), spray chamber was cyclone spray and nebulizer was Burgenar trace. The results were expressed in µg/g of dry plant.

Production and characterization of Co and Ni nano particles

The cobalt chloride and nickel chloride ($CoCl_2$. $6H_2O$ and $NiCl_2$. $6H_2O$) were purchased from Sigma Aldrich USA, and 1-10 phenanthroline was purchased from Fluka. All solvents were of analytical reagent grade and were used without further purification.

For the synthesis of complex of cobalt, 0.5 M solution of 1-10 phenanthroline and 0.5 M solution of cobalt chloride were separately prepared in 1-propanol. The 1-10 phenanthroline solution was taken in dropping funnel and very slowly dropped to the cobalt chloride solution with constant stirring at a temperature of 40 - 50°C. The pink precipitate of cobalt/ 1-10 phenanthroline complex appeared after almost one third (⅓) of 1-10 phenanthroline solution was added to cobalt chloride solution; the adding of the 1-10 phenanthroline solution to the salt solution was continued till complete precipitate formed in the reaction mixture. The precipitate was then filtered and washed two times with 1-propanol to remove the un-reacted 1-10 phenanthroline/ cobalt chloride. The precipitate was dried under IR lamp and then under vacuum. The complex was taken in a two-neck flask and was kept in tube furnace for decomposition. One side of the flask was connected to argon cylinder and the other was used as outlet for argon and decomposition gases. The temperature of the furnace was raised to 500°C at a heating rate of 0.5°C min^{-1} and the contents were kept at 500°C for 24 h and then allowed to cool to room temperature under an inert atmosphere of argon gas to yield Co nano particles.

Same procedure was used for the preparation of Ni nano particles. The particle morphology and size was studied by SEM (Scanning Electron Microscope- Zeiss Supra 50VP with EDS Oxford), TEM (Transmission Electron Microscope- FEI Tecnai F20 S-TWIN 200 FEG) and XRD. The X-ray diffraction pattern of the particles powders were collected with PANalytical, Netherlands, diffractometer (Model 3040/60 X^{l} pert PRO) equipped with a Cu Kα radiation source. Using Scherrer formula, based on line broadening, the mean crystal sizes of the powders were determined (Niasari et al., 2007).

Catalytic gasification of water hyacinth by Co and Ni nano particles

For gasification experiment, 5.315 g oven dried plant was mixed with 0.013 g Co (0.24% of sample) and 0.003 g Ni (0.05% of sample) nano particles in a 100 ml beaker. The beaker was placed in PARR-2843 reactor. Argon was flushed through reactor to remove oxygen content. The reactor was heated up to 400°C for 15 min. The gaseous samples were collected at 50, 100, 200, 300 and 400°C, and were analyzed by using online Gas Chromatography Mass Spectrometer (Hewlett-Packard [Palo Alto, A] 5890 series II gas chromatograph with Hewlett-Packard 5972 mass selective detector).

Fermentation of water hyacinth by yeast for bioethanol production and its identification by GC and GC-MS

Five grams water hyacinth was hydrolyzed by a modified procedure with diluted sulfuric acid (Hamelinck et al., 2005) because yeast (*S. cerevisiae*) is able to directly ferment water hyacinth hydrolysate after neutralization. A low sulfuric acid concentration (1%) was used for one hour reflux at 110°C. One gram common commercial yeast was mixed with above refluxed extract. This mixture was placed at room temperature for three days as described by Masami et al. (2008). After three days, the extract was filtered and after extraction with chloroform it was analyzed by GC-MS. The result showed presence of ethanol and acetic acid.

Photo catalyst production, characterization by TEM and XRD

For the preparation of polycrystalline nano particles of TiO_2 Fluka $TiCl_4$ (98% purity, Analytical grade) was diluted up to 15% (1.33 M) in 15% H_2SO_4 in distilled water. A light yellow colored solution was obtained with pH of - 0.75. The solution was stirred for two hours at room temperature. The NaOH solution (3 M) was added drop wise (controlled through HPLC pump). The resulting solution was continuously monitored for pH. When the pH reached - 0.11, the light yellow coloration disappeared and a transparent solution was formed. The drop wise addition of NaOH was continued until the pH of the resulting solution becomes 0.85. At this pH, white precipitate was obtained. The pH of the white precipitate was further increased to 2 by the addition of NaOH which was later stopped. It was then washed with distilled water to remove all the NaOH solution. The material was dried overnight at 100°C. The TiO_2 powder thus obtained was calcined at 500°C for 6 h. The particle morphology and size was studied by TEM (Transmission Electron Microscope- FEI Tecnai F20 S-TWIN 200 FEG) and XRD. The X-ray diffraction pattern of the particles powders was collected with PANalytical, Netherlands, diffractometer (Model 3040/60 X^{l} pert PRO) equipped with a Cu Kα radiation source. Using Scherrer formula, based on line broadening, the mean crystal sizes of the powders were determined.

Production of methane by photo catalysis and analysis by GC

A clean, dry, glass tube fitted with a stopper was used for photocatalyst experiment (Figures 7 and 8). Ten grams fresh biomass of water hyacinth was crushed, dried with blotting paper and placed in this glass tube with 0.2 g anatase titanium dioxide. This apparatus was placed in bright sunlight for six hours. The gaseous sample was tested by burning on flame and by using GC (Figures 7 and 9). After three days these samples were analyzed by GC (Gas Chromatograph Model Varian CP-3800). The result showed the presence of methane, methanol and ethanol (Figure 1).

RESULTS

Analysis of water hyacinth and other parameters

Fresh weight, dry weight, moisture content, ash content and crude fibre content for five samples of water hyacinth were assessed. The results were 59.2 ± 14.63 g fresh weight, 4.8 ± 1.16 g dry weights, 3.6 ± 1.0 g of ash, and 90.8 ± 0.40% moisture of fresh weight. Dry plants contain 77 ± 2% ash and 1.4 ± 0.48% crude fibres. Elemental concentrations of boron and metals in water hyacinth measured by ICP-AES were 100.66 ± 3.68 B, 5979 ± 2.44 Al, 56 ± 0.81 Cu, 1218 ± 1.63 Fe, 8444 ± 3.26 Mg, 898 ± 0.81 Mn, 216 ± 1.63 Mo, 10 ± 0.81 Ni, 158 ± 0.81 Ti and 285 ± 0.82 Zn, respectively, in µg/g of dry plant.

Gasification and pyrolysis experiment

On gasification, charcoal 56.83% of dry weight and gases

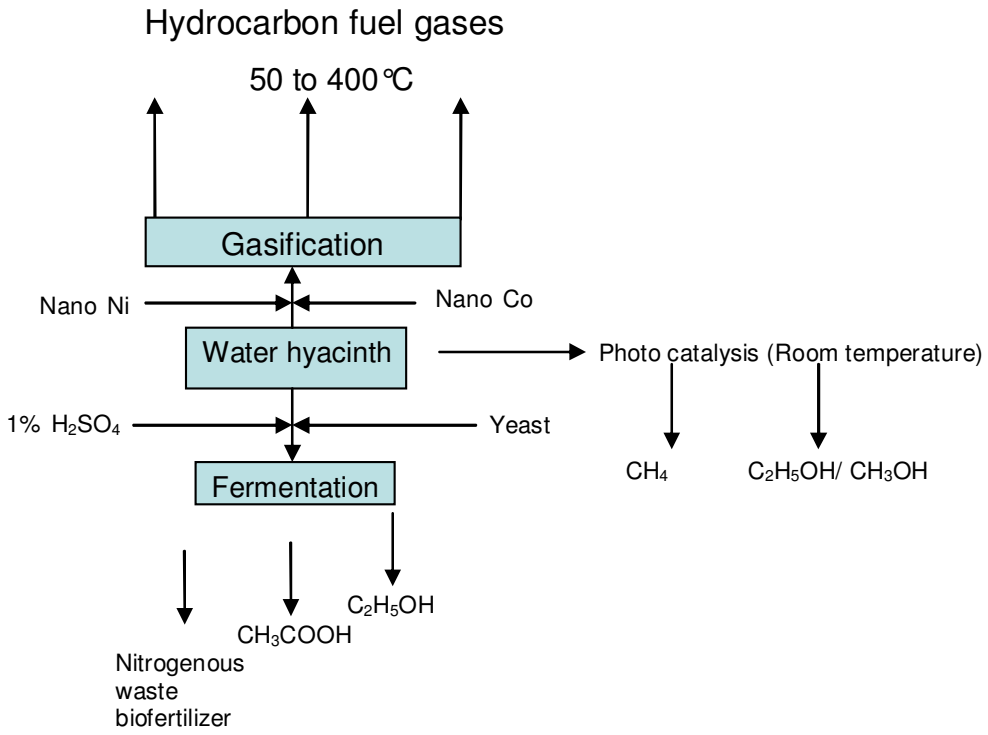

Figure 1. Summary of water hyacinth as a source of Biofuels

Table 1. Gaseous products variations with temperature.

S/N	m/z	Peak identification	Experimental temperature for gaseous samples and percentage of product gases and radicals				
			50°C	100°C	200°C	300°C	400°C
1	12	Carbon gas	-	-	-	-	2.38%
2	14	-CH_2- Methylenic group	6.12%	16.68%	2.36%	7.68%	1.82%
3	15	CH^+_3 Methyl group	-	-	0.03%	-	2.18%
4	16	CH_4 Methane	2.82%	6.67%	2.41%	4.78%	4.85%
5	18	H_2O	-	4.44%	4.30%	4.17%	5.24%
6	20	H_2C =BH	-	1.30%	12.86%	4.08%	8.01%
7	28	CH_2 = CH_2 (Ethene)	45.52%	24.67%	20.84%	21.04%	19.74%
8	29	$CH_3CH^+_2$ (Ethyl group)	-	-	-	-	1.72%
9	30	C_2H_6 (Ethane)	-	-	-	-	0.37%
10	32	CH_3OH (Methanol)	-	24.67%	2.37%	17.70%	1.43%
11	40	C_3H_4 (Propyne)	45.52%	21.20%	34.79%	21.04%	26.09%
12	44	C_3H_8 (Propane)/ (CH_3CHO) Acetaldehyde	-	0.33%	19.99%	19.47%	26.09%

43.16% of dry weight was obtained. These gaseous samples were collected at 50, 100, 200, 300 and 400°C. These were analyzed on GC-MS and the results are given in Table 1. At 50°C ethene and propane, at 100°C ethene and methanol, at 200°C ethene and propyne, at 300°C ethene, propyne and propane, while at 400°C ethene, propyne, propane were produced. Due to increase of temperature, increase in molecular weight of product gases was observed (Figures 3 - 5).

Fermentation of water hyacinth

Fermentation of water hyacinth by *S. cerevisiae* was used for ethanol production. The reaction temperature of 110°C for acid digestion of cellulosic fibers was used. Chloroform based extract was analyzed with GC-MS. The results showed C_2H_5OH (m/z = 46, with concentration of 55.20%), CH_3COOH (m/z = 60, with concentration of 41.66%) and HC $(OH)_2$-HC^+OH (m/z = 77, with concen-

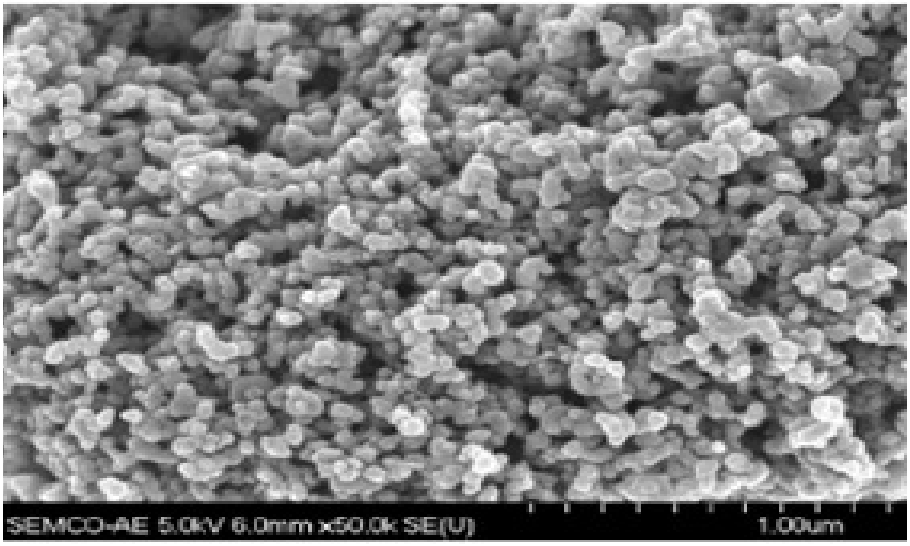

Figure 2. SEM image of cobalt-nano particles.

tration of 3.12%).

Photocatalysis of water hyacinth

Titanium dioxide nano particles were characterized by using TEM and the results are presented in Figure 6. TEM show uniform structure with maximum size of 3 nm. The gas chromatographic results show the presence of methane (53.19%), methanol (37.23%) and ethanol (9.57%). NAS (1976) suggests that 1 ha of water hyacinth can produce more than 70,000 m^3 of biogas (70% methane, 30% CO_2). Graig A. Grimes, used titanium dioxide to convert a mixture of carbon dioxide and water vapors to methane. They reported higher yield of methane than previously reported (FuturePundit: Nanotubes for Photocatalysis Produce Methane; 10th July, 2009, http://www.futurepundit.com/archives/006019.html). By using sun light energy, titanium dioxide converted CO_2 and moisture to methanol and ethanol (Figures 7, 8 and 9).

DISCUSSION

The water hyacinth was collected from Taxila, situated at 33°45'0"N 72°48'36"E, the north-western edge of the Punjab province of Pakistan. Our study is based on analysis of metal hyper accumulator, its different parameters, catalytic gasification, fermentation and photocatalysis of biomass. Figure 1 describes the summary of our experimental work that is; with the change of conditions various products were formed.

The results of fresh weight, dry weight, moisture content, ash content and fibre content for five samples of water hyacinth were similar with the previous studies (Little and Henson, 1968; Okoye et al., 2002). All these values are showing very minor variations and were calculated by the formulas described by Okoye et al. (2002). El-Hendy (2008), studied modeling of heavy metals removal from municipal landfill leachate by using living biomass of water hyacinth. They observed the increase in concentration of total heavy metals of water hyacinth. Our results are showing its ability as hyperaccumulator and high metal content in soil or water of its habitat. Analytical data also shows that it contains suitable amount of titanium (Ti) which is used in the preparation of photocatalyst. This amount of Ti like other metals can be extracted/ leached down by desorption with HCl by using its dry mass. Metal hyperaccumulation depends upon the impact of various factors, such as microclimate, hydrology, soil physics, soil chemistry and soil biology (Liao and Chang, 2004). Our study provides quantitative information about metals absorbed by water hyacinth from soil of Taxila and lays the foundations for more detailed research work. The most important properties related to the thermal conversion of biomass are various but important are moisture content, ash content and volatile matter content. The moisture content depends on water's weight. It can affect the value of biomass. Volatile matter is obtained from 400 - 500°C. Hydrocarbon products of gasification depend upon volatile matter of biomass. The total ash content also affects gasification and combustion at high temperature (Quaak et al., 1999). In gasification/pyrolysis experiment, water hyacinth is gasified, pyrolysed and then reformed into hydrocarbons and alcohols. Gasification and pyrolysis is the thermal decomposition of solid biomass at a temperature of 650 - 800K at 1 - 5 bars pressure in the presence/ absence of air to yield liquid, solid charcoal and gaseous compounds (Navarro et al., 2009). Reddy and Tucker (1983) gasified water hyacinth at 800°C. Our

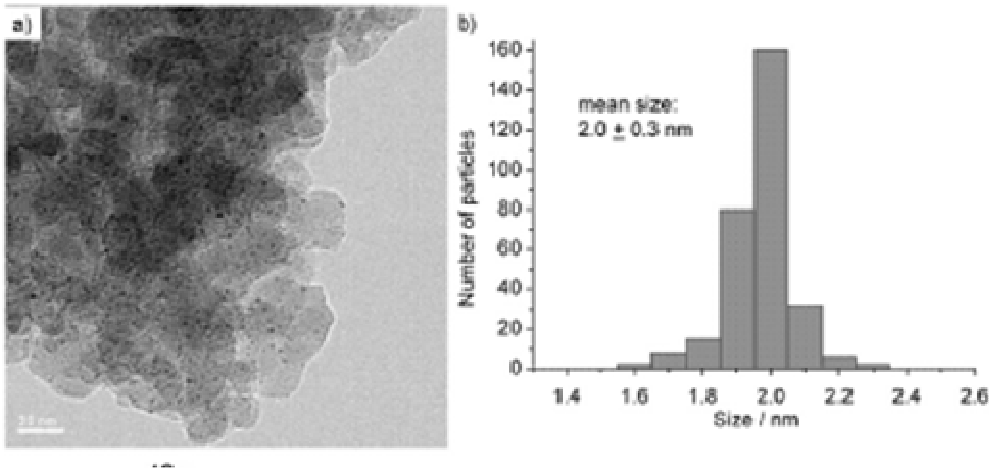

Figure 3. TEM image of nickel-nano particles.

results show the product formation at low temperature is due to high activity of Co and Ni nano particles.

Gasification converts carbonaceous material such as coal, petroleum or biomass into CO and H_20 (syn gas) by heating the raw material at high temperatures with a controlled amount of oxygen and/ or steam; syn gas itself is a fuel. It may contain smaller quantity of CO and CH_4. It is the carbon monoxide (CO) fraction of syn gas that is converted into ethanol and other hydrocarbons gases as it is passed over a catalyst. Carbonaceous matter can directly produce alcohols and hydrocarbons in the presence of catalyst. Nano particles converted more rapidly this material to syn gas and than into other fuels. In gasification, Ni improves the biomass fast-pyrolysis process and its economics (Aznar et al., 1998; Li et al., 2009). The ICP analysis showed that water hyacinth plant contains Ni 10 ± 0.81 µg/g of dry plant. It played its role in gasification and added Ni nano particles accelerated the same reaction. The gaseous products are obtained at 50°C. The un-saturation and molecular size of products was increasing by increasing temperature. In reforming of gasification products Ni, Co, Fe, Cu, Mg, Mn, Ti and Zn played important role due to their Fischer-Tropsch hydrogenation activity and also as promoters. Analytical data of water hyacinth showed that it already contains these elements in excess that is why gasification and pyrolysis is happening at very low temperature. Nickel catalyst, due to an easy dissociation of CO, possessed too much hydrogenation activity, resulting in high yields of CH_4. Same catalytic activity is possible with cobalt (Co). Cobalt is preferred for production of paraffins, as it gives the highest yields for high molecular weight hydrocarbons from clean feedstock (Vannice, 1975). Cobalt and its nano particles were supported on by an oxide base like silica, alumina and titania. Fresh plant contains 0.06% P_2O_5 and 0.20% K_2O. On a zero-moisture basis, it contains 24.2% ash. The ash contains 28.7% K_2O, 1.8% Na_2O, 12.8% CaO, 21.0% Cl, and 7.0% P_2O_5 (Matai and Bagchi, 1980). The oxides of Al, Si, Ti and Ca acted as support to Co nano particles and water hyacinth is pyrolysed at low temperature and atmospheric pressure. The variations in the product gases were due to Ni and Co nano particles.

We used Co and Ni nano particles. The SEM image (Figure 2) and TEM image (Figure 3) demonstrated the morphology as well as crystallite size of metallic nano particles which were synthesized through hydrothermal method. The images indicated that the particles are uniform regular spherical sponge-like in shape in both the cases (Co and Ni) and fall in the size range 2 - 90 nm. This is comparable to the crystallite size calculated from XRD by applying Sherror formula. The XRD has given prominent peaks for the metallic nano particles of nickel and cobalt. The XRD pattern of fresh cobalt nano particles was studied and from the data and cubic structure for cobalt nano particles was obtained by using the standard ASTM XRD files. The XRD peaks corresponds to the indices (111) and (200). The peaks obtained for nickel nano particles are consistent with the indices (111), (200) and (222) of pure phase centered cubic with 2Θ at 44.4, 51.8, and 76.4°, respectively, for the above mentioned indices and it could be concluded that the nano particles of nickel prepared through this method were pure with a controlled phase of FCC structure.

Table 1 shows the gaseous products variations with temperature. At 50, 100, 200, 300 and 400°C, C_2H_4 is in higher percentages. The reaction rate and nature of product depends on temperature, particle size, particle morphology, pressure, surface area of nano particles and nature/ chemistry of biomass (Aye and Yamaguchi, 2006; Davidian et al., 2006; Kimura et al., 2006; Svoboda et al., 2007; Swierczynski et al., 2007; He et al., 2008). We proposed here that the Ni-nanoparticles act as a green catalyst for selective reduction to give the corresponding alcohols in good yields (Kidwai et al., 2006).

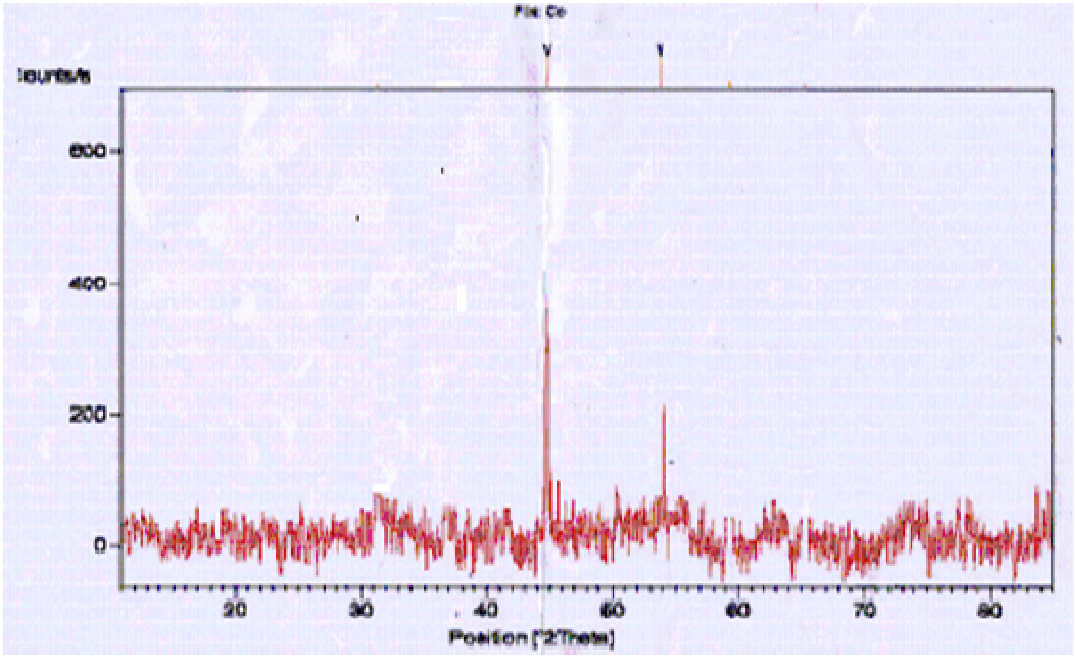

Figure 4. XRD spectrum for cobalt nano particles.

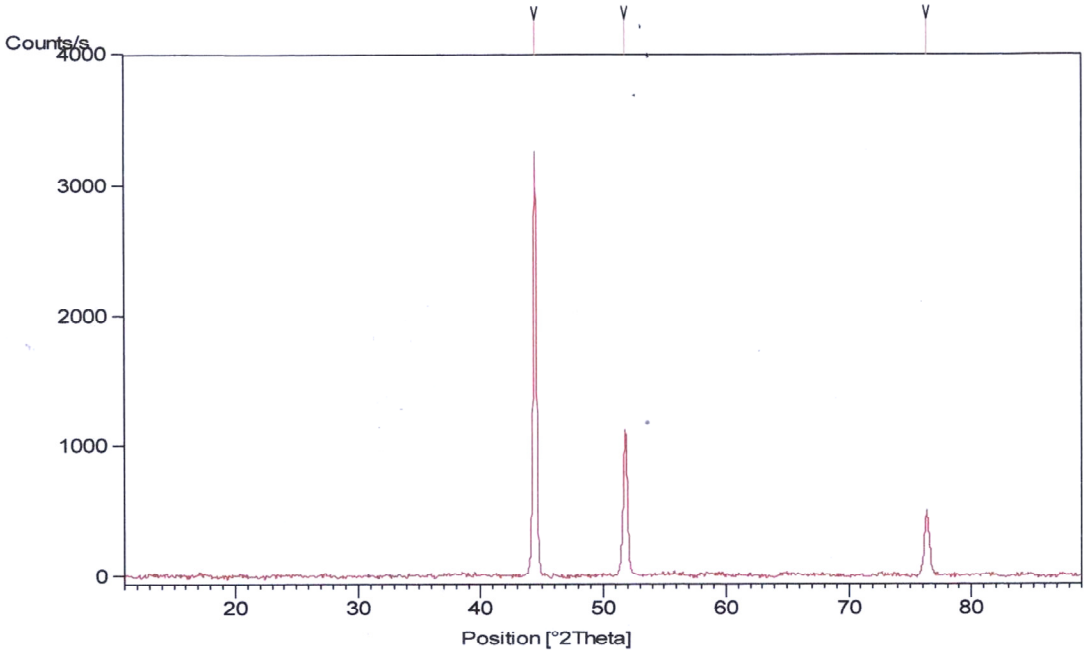

Figure 5. XRD Spectrum for nickel nano particles.

Photocatalysts act as strong oxidizing agents. They create electronic holes in order to break the organic matter to carbon dioxide and water in the presence of light. The photocatalytic properties of TiO_2 were discovered by Akira Fuji Shima in 1972 and the process on the surface of TiO_2 was called Honda- FujiShima effect. Titanium dioxide is a semi conducting material which can be chemically activated by light. Anatase shows the highest photo activity under UV light. The benefits of applying nanotechnology to catalysis include improved activity, lifetime, resistance to poisoning and other novel abilities. Photocatalytic activity (PCA) is the ability of a material to create an electron hole pair as a result of exposure to ultraviolet radiation. The resulting free-

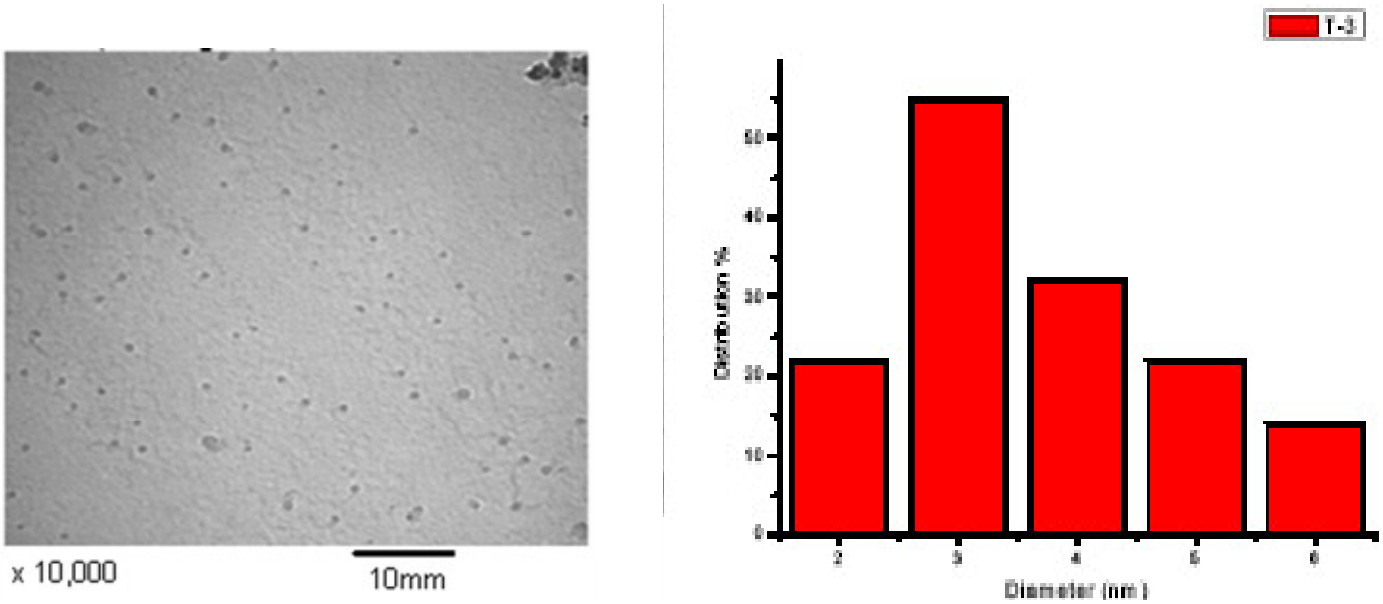

Figure 6. TEM image of TiO_2 nano particles

Figure 7. Apparatus for gas samples of photo catalytic experiment.

radicals are very efficient oxidizers of organic matter. Photocatalytic activity in TiO_2 has been extensively studied because of its potential use in sterilization, sanitation and remediation applications. The ability to control PCA is important in many applications. Low PCA is required in utilizing TiO_2 in paints, pigments and in cosmetics. The oxidative behavior of photocatalyst oxidizes hydrocarbons to alcohols. The -OH radical produced by anatase can decompose a variety of organic compounds. The UV illumination of titanium dioxide leads to the formation of powerful agents with the ability to oxidize and decompose many types of bacteria, organic and inorganic materials. Large quantities of Ti (158 ± 0.81 µg/g of dry plant) as TiO_2 is present in water hyacinth, accelerate oxidation process. The photo catalyst in light increased conversion of biomass into CO and H_2O. The metals present in biomass as oxide acts as catalyst to produce CH_4 and CH_3OH. On oxidation (by TiO_2 photocatalyst or by already present in plant) CH_4, C_2H_5OH and CH_3OH were obtained.

Plant based lignocellulosic material contains a mixture of carbohydrate polymers (cellulose and hemicellulose) and lignin. Carbohydrate polymers are tightly bound to lignin mainly through hydrogen bonding but also through some covalent bonding. Cellulose is a linear polymer which contains glucose linked through β-1,4-glycosidic bonds. Hemicellulose is heterogeneous polymers of pentoses, hexoses and sugar acids. Lignin is a very complex molecule. It is an aromatic polymer constructed of phenyl propane unit. Cellulose is broken into glucose by using enzymes of yeast. It is converted into ethanol by enzymes. Hemicellulose is hydrolysed into xylose and mannose among others. With enzymes like xylose isomeriase, these are converted into ethanol and acetic acid e.g. we can not obtain more than 90 - 95% ethanol but some byproducts like acetic acid and glycerol are also possible (Kosaric et al., 1983; Brandberg, 2005). The GC-MS analysis of product in which fermentation process was used showed that commonly available yeast (*S. cerevisiae*) can produce sufficient quantity of ethanol and acetic acid, and uses optimum temperature between 30 to 35°C. Same temperature range is suitable for simultaneous saccharification and fermentation. The two most

Figure 8. Apparatus for photo catalysis of water hyacinth.

promising processes for industrial production of bioethanol from cellulosic materials are two-stage dilute-acid hydrolysis (a chemical process) and simultaneous saccharification and fermentation (an enzymatic process). Hydrolysis for several days was considered necessary in enzymatic method while a few minutes are enough for acid hydrolysis. The enzymes like cellulase are very expensive than 1% H_2SO_4. Distillation is a very useful technique for separation of ethanol from other products of fermentation. However in ethanol blending with gasoline the water content of alcohol must be reduced to less than 1% by volume, which is not possible by distillation (Wilkie et al., 2002). Our technology is cost effective; rate of hydrolysis is very fast and degradation of unnecessary nutrients is also very high as compared to other methods as reported by Nag (2008).

It is suggested that the methane might be raw material for producing larger alkanes and other compounds. Perhaps nano-materials will provide efficient means to capture solar energy for this purpose too. The higher activity, smaller size and larger surface area of photo-catalyst are responsible oxidation of carbon based biomass to carbon dioxide. The higher moisture content helped the preparation of methane, methanol and ethanol. Jones et al. (2007) support this idea of photocatalysis.

Conclusion

1. Water hyacinth (*Eichhornia crassipes*) is a good tool for cheap industrial production of biofuels.
2. After fermentation and photocatalysis, solid residue is

Figure 9. Burning of photo catalytically produced methane.

rich in N, P and proteins can be used as biofertilizer.
3. Gasification waste is a best source of carbon for soil fertility.

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