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Use of Kinnow Peel as a Source of Biofuels and Carbon Nano Fibers

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Abstract: Only alternative and cheap source of energy which can be made easily be available to the world is bioenergy. Our experiment included the conversion of Kinnow/Orange peel into biofuels. In the first step Kinnow peel was gasified by using Cobalt oxide nano catalyst at 300, 400°C and at atmospheric pressure. Catalytic gasification yielded 60% liquid extract, 28% fuel gases, 1-5% tar and 10-12% charcoal. Gaseous products contain 3.80-53.03% ethene, 13.15-29.51% methanol, 1.28-1.77% propyne, 6.32-28.67% propane and 3.89-4.59% methane. In second step liquid extract of Kinnow peel obtained from gasification, on etherification gave ethyl ester (biodiesel). This study reports an interesting finding that Kinnow peel as could be used for not only the production of biodiesel, biomethanol, hydrocarbon fuel gases and Char as a source of carbon nano fibers. The world today is producing several million tons of Kinnow peel. The XRD spectrum of char or ash shows the formation of carbon fibers. The technology could be utilized to produce alternate energy.

Keywords: kinnow (orange), catalytic gasification, Co oxide nano particles, biofuel, nanotechnology

Introduction

Pakistan is the sixth largest producer of Kinnow (mandarin) and oranges in the world, with 2.1 million tons. Pakistan is also the largest producer of 'Citrus Reticula' variety (Kinnow), this unique variety of citrus is indigenous to this part of the world. According to an estimate approx. 95 percent of the total Kinnow produced all over the world is grown in Pakistan [1].

When biomass is burnt lot of heat is produced which can be used for various purposes. The biomass can also be converted into fuels like ethanol and biodiesel that can be used as the fuels for the vehicles. Methane produced from the biomass is the major component of natural gas which is being used. The 220 billion dry tons of annual available biomass potentially represents the world's largest sustainable energy source. As a result, it is becoming one of the most important renewable energy sources in our planet's immediate future [2].

Gasification and pyrolysis is the thermal decomposition of solid biomass at a temperature of 650-800 K at 1-5 bars in the absence of air to yield liquid extract, solid charcoal and gaseous compounds [3]. On gasification million tons of Kinnow waste may produce million tons of liquid extract. On esterification of liquid extract million tons of Kinnow waste may gives several million tons of biodiesel and charcoal. A computer based model predicted that a high gas production can be achieved during gasification when a high temperature (750°C) was applied [4]. The use of catalysts during biomass gasification produce char gases and reduces the tar yield obtained when the gasifier is operated at lower temperature [2]. Basily, et al., [5] converted oil residues into unsaturated hydrocarbons by using nano catalyst. For better fuel formation a pyrophoric catalyst is required. In this regard, cobalt has extensively been used for catalytic gasification. He et al. [6] studied the influence of catalyst and temperature on yield and product composition. They used temperature range 750-950°C. However, reactions catalyzed by Co were very slow owing to the low surface area of the catalyst. The use of Co metal nano particles as catalysts in gasification is more popular [7]. Mahmood and Hussain [8] have employed nano particles in catalysis. Cobalt nano particle catalysts may be influenced by their size, morphology and structure. Co or Co oxide nanostructures are known to be effective catalysts ([9]; [10]; [11]). Cobalt nano particles, in particular being cheap, need mild reaction conditions for high yields of products in short reaction times as compared to the traditional catalysts.

For the analysis of biofuels we used already documented techniques like GC-MS (Gas Chromatography-Mass Spectrometry) ([12]; [13], GC (Gas Chromatography) [14] and FTIR (Fourier Transform Infra Red spectroscopy). We studied properties of nano particles by TEM (Transmission Electron Microscopy), SEM (Scanning Electron Microscopy) and XRD (X-Rays Diffraction) as already documented in literature [15].

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In present study we converted Kinnow waste into hydrocarbon fuel gases, biodiesel and charcoal/char. Previously gasification was done by using Cobalt oxide catalysts at high temperature [8] similarly expensive reagents were used by Guru, et al., [16]. We converted Kinnow peel to biofuels at low temperature. The byproduct biochar/charcoal can be used as biosorbent for waste heavy metal's removal from water. Gasification of biomass gives different carbon structures. Biochar is used as fertilizer for soil. Its adsorption of organic matter from soil facilitates interaction between the biochar and mineral phase of soil [17].

Materials and Methods

Synthesis of Nano particles: Nano particles of cobalt oxide were prepared by sol gel method by using $CoCl_2.H_2O$ (AR grade). The technique used was same as described Mahmood et al (2010); Mahmood and Hussain (2010). After calcination and grinding the particles were characterized by SEM (Scanning Electron Microscope) Zeiss Supra 50VP with EDS Oxford), XRD (PANalytical, Netherlands, diffractometer (Model 3040/60 X! 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 & particle size was measured) ([18]; [8]; [19]).

For nano catalytic gasification 100g of Kinnow peel's sample was taken while Cobalt oxide nano particles were only 0.010g. The sample was heated in carbolite furnace up to 400°C. The gaseous samples were collected at 300°C and 400°C. Gasification procedure which we used is described by Mahmood et al., (18), Mahmood and Hussain (8) Mahmood (19) and Hussain et al., (20). The Figure 2 shows that a flask of sample is placed in the center of furnace and out of the furnace a glass tube is coming it also shows the experimental set up. Figure 1 show that out of furnace gases are burning with flames. It shows the presence of hydrocarbon gases produced as a result of gasification. A U shape tube was used for the sample collection of bio oil and gases. Gaseous samples were collected by evacuated shilling tubes. Analysis of gaseous samples was carried out by Gas Chromatography Mass Spectrometery (GC-MS-Hewlett-Packard [Palo Alto, A] 5890 series II gas chromatograph with Hewlett-Packard 5972 mass selective detector) [13] the results were recorded. Volume of liquid extract, gases and char/charcoal were measured. Esterification of liquid extract/bio oil obtained from gasification was done by the procedure as described by Mahmood and Hussain [8]. The samples of product oil were analyzed by FTIR as described by Hussain et al., [20]. The pH of extract/bio oil was measured by pH meter. XRD analysis of char was done by PANalytical, Netherlands, diffractometer (Model 3040/60 X! pert PRO) equipped with a Cu Kα radiation source as described by Mahmood, [19].

Experimental conditions are given in figure 1 and 2.

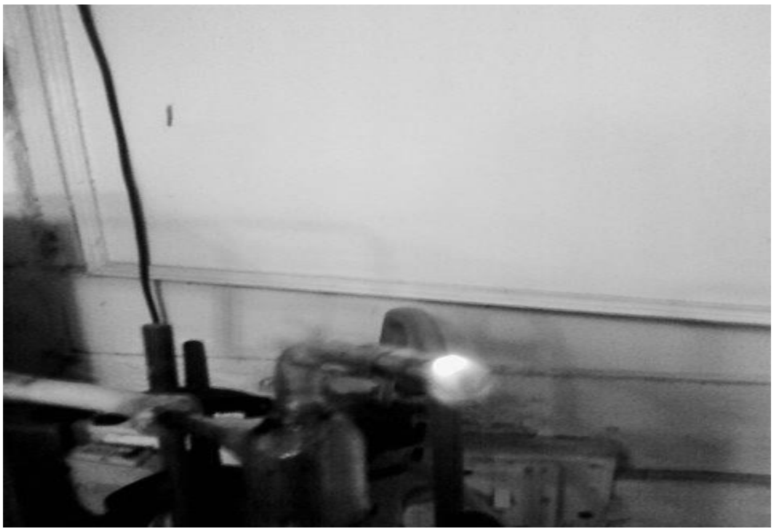


Figure 1: Tube with burning gaseous sample produced as a result of nano catalytic gasification

Figure 2: Flask with burning ash placed in the center of furnace

Results and Discussion

The present study was based on nano catalytic pyrolysis, gasification, and esterification. Pyrolysis is the thermal decomposition of solid biomass at high temperature and pressure [3]. In this study, low temperature due to high activity of Cobalt oxide nano particles was used. The thermal gasification produces hydrocarbons at 1000°C in the absence of air. The catalytic gasification decreased reaction temperature up to 650°C. The simplest type of gasification is the fixed bed countercurrent gasification. The major advantages of this type of gasification are its simplicity, high charcoal burnout, and internal heat exchange that led to low gas-exit temperatures and high gasification efficiencies [21]. Cobalt nano particles due to high reactivity and higher surface area decreased the reaction temperature and activation energy. In the present experiment, gasification was carried out at 300 & 400°C which is the lowest possible temperature (Table 1 & Figure 8). Thermo-dynamic calculations in the degradation process showed that the cleavage of C-O bond took place at 288°C. Generally, thermal decomposition proceeds through either free radical or carbonium ion mechanism. Under these conditions of thermal decomposition, GC-MS analysis showed that product are made up of C numbers ranging from C=1 to more than 20 ([22]; [5]). On gasification, organic compounds were converted into CO_2 and H_2O. Cobalt reacts to produce CoO after converting CO_2 to CO and H_2O to H_2. Now $CO+H_2$ are synthetic (syn) gas and Co is already known as Fischer-Tropsch catalyst for conversion of syn. gas to hydrocarbons. The gaseous products of Kinnow waste gasification thus obtained were analyzed by GC-MS and the results were given in Tables 2 and 3. Reddy and Tucker [23] gasified water hyacinth plant at 800°C. In the present investigation, low temperature due to high activity of Co nano particles was used. For their characterization SEM (Figure 5) and XRD (Figure 4) were used. SEM image demonstrates the morphology as well as crystallite size of metallic nano particles which were synthesized through hydrothermal method. The image indicated that the particles were uniformly regular spherical sponge like in the shape of Co and fall in the size range of 2 – 90 nm. This is comparable to the crystallite size calculated from XRD (Figure 4) by applying Sherror formula. The XRD (Figure 4) has given prominent peaks for the metallic nano particles of cobalt. The XRD pattern of fresh cobalt oxide nano particles was studied and from the data, cubic structure for cobalt oxide nano particles was obtained using the standard ASTM XRD files. The XRD peaks corresponds to the indices (111) and (200). It could be concluded that the nano particles prepared through this method were pure with a controlled phase of FCC structure. Various studies reported that Co nano particles are used in catalytic gasification of biomass. The temperature, particle size, particle morphology, pressure, surface area, nature of nano particles and nature/ chemistry of biomass were responsible for product percentage, nature of product and reaction rate ([4]; [24]; [25]; [26]; [27]; [6]. The nano particles act as green catalyst for selective reduction of the aldehydic group in the presence of other functional groups. For example, NO_2, CN and alkenes gave the corresponding alcohols in excellent yields [7] (Tables 2 and 3). These results were supported by previous studies [28]. The preparation of hydrocarbon gas like ethylene is also supported by Basily, et al., [5]. The same study confirms the production of alcohols from these unsaturated hydrocarbons. Formation of CaO due to oxidation of Ca may result into formation of unsaturated hydrocarbons from organic compounds. Because according to Basily, et al., [5] CaO acted as nano catalyst. The liquid extract of Kinnow waste containing small quantity of tar and showed acidic pH (4.13) due to carboxylic acids. After esterification the FTIR spectrum (Figure 4) showed that first percentage transmittance peak was at 1633.10 wave number cm^{-1} while the other was at 3304.83 wave number cm^{-1}. First is showing C=O linkage of ester. Voort, et al. [29] described that the peak between 1500 to 2000 showed ester linkage but between 3000 to 3500 is of –OH or hydrocarbons. According to Lima et al., [30] FTIR spectrum of biodiesel peaks is between 3000 and 4000 and showed C-OH bending. During pyrolysis of biomass hydrocarbons are produced and are oxidized to alcohols and later to carboxylic acids by catalyst. Alcohols are reduced to hydrocarbons by catalyst. The alcohols react with carboxylic acid to give esters as shown in FTIR spectrum (Figure 4). The liquid extract of Kinnow waste was esterified with ethyl alcohol and NaOH at low temperature as described by Mahmood and Hussain [8]. Esters presence was verified from FTIR spectrum (Figure 4).

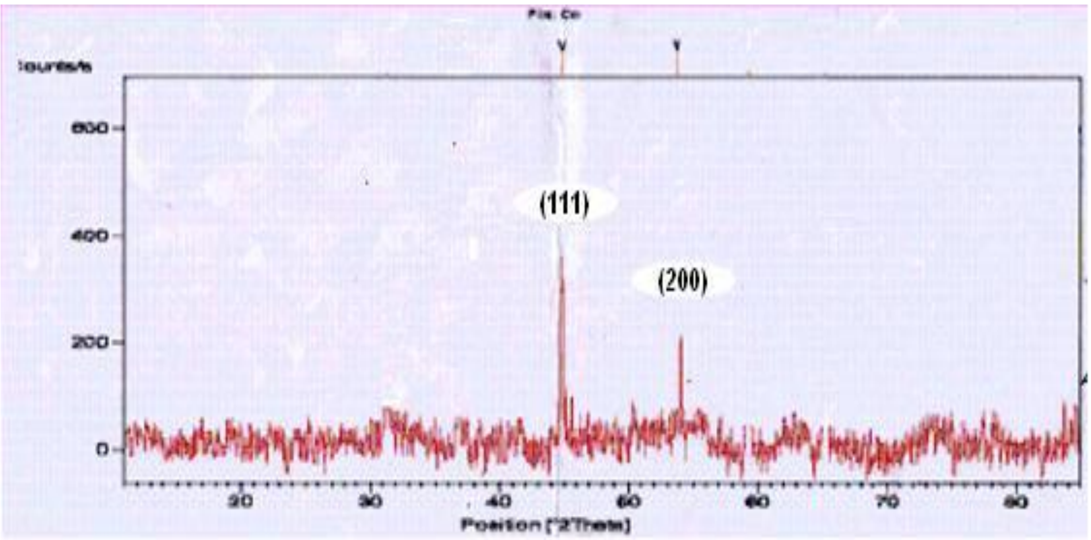


Figure 3: XRD Spectrum of Cobalt oxide Nano particles

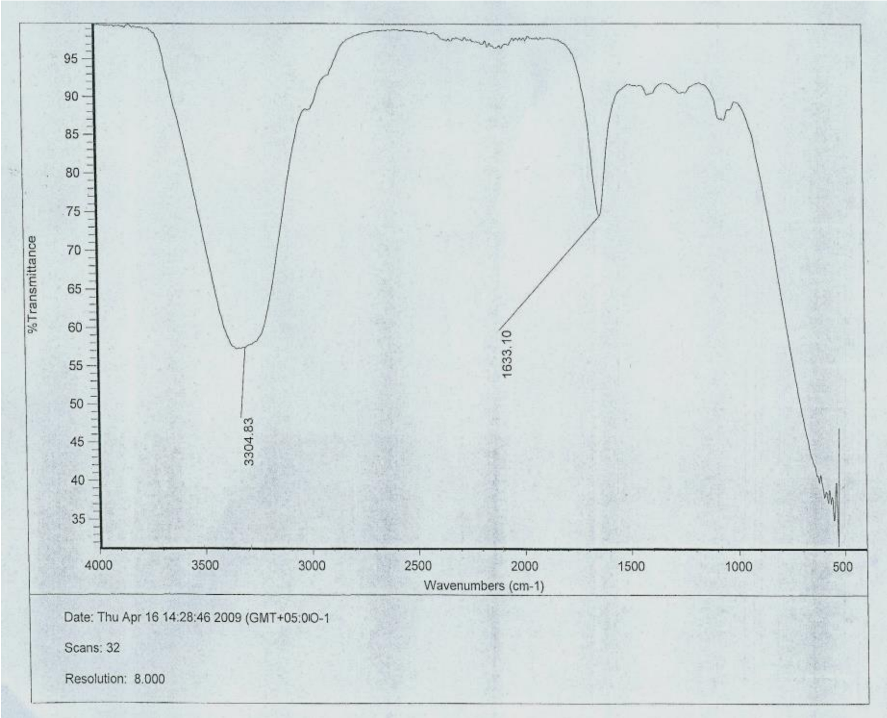


Figure 4: FTIR Spectrum of bio oil sample

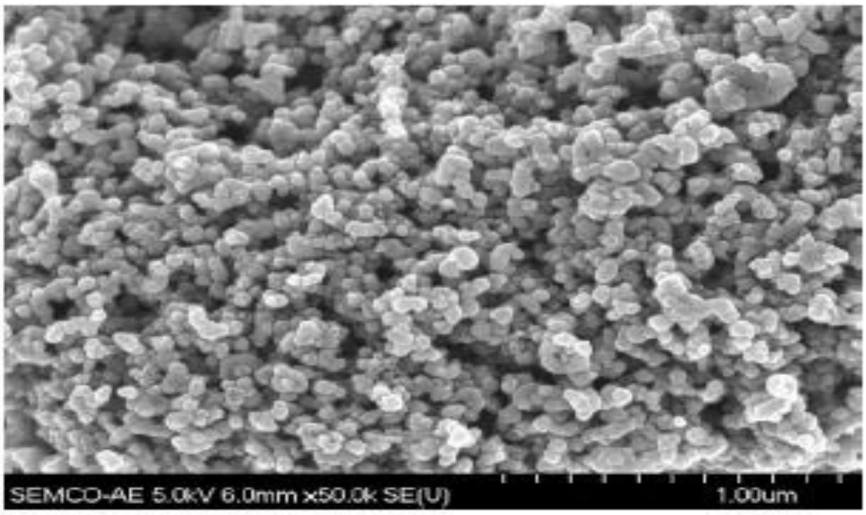


Figure 5 SEM of cobalt oxide nano particles before gasification

Table 1: Results of Kino waste gasification

Weight of Kinnow waste = 100g Weight of Cobalt oxide nano particles = 0.010g Temperature = 300°C Temperature = 400°C,		
Gaseous product = 28%	Liquid product = 60% With pH = 4.13 Tar = 1-5%	Solid (charcoal) product = 10-12%

Table 2: Results of GC-MS of gaseous sample taken at 300°C.

No of Peaks	Fragments	m/z	Abundance	Percentage
1	Methane (CH_4)	16	60774	4.21%
2	Ethene (C_2H_4)	28	8388096	58.17%
3	Methanol/(CH_3OH)	32	4255232	29.51%
4	Propyne (C_3H_4)	40	256512	1.77%
5	Propane (C_3H_8)	44	911616	6.32%

Table 3: Results of GC-MS of gaseous sample taken at 400°C.

No of Peaks	Fragments	m/z	Abundance	Percentage
1	Methylenic group	14	826624	4.31%
2	Methane (CH_4)	16	746176	3.89%
3	Ethene (C_2H_4)	28	8388096	3.80%
4	Methanol/(CH_3OH)	32	2672128	13.95%
5	Propyne (C_3H_4)	40	246976	1.28%
	Propane (C_3H_8)	44	5491200	28.67%

The char/charcoal produced by the gasification was analyzed by XRD. Generally carbon nano tubes/fibers or coil like material, is obtained at very high temperature but due to Cobalt oxide nano particles it was achieved at low temperature i.e. at 400°C. Figure 6 and 7 are showing XRD spectrum of char/charcoal. These figures show that a broad reflection peak at 22-23.5° corresponds to (002) planes of carbon nano coils/fibers/tubes. The broadening of peak is an indication of very small amorphous forms of the samples. The particle size as calculated by using Scherrer formula. The average particle size is in nm. No other impurity peaks are observed in XRD which indicates that Kinnow waste's ash can is potentially be used for the large scale production of relatively pure carbon nanocoils/fibers/tubes.

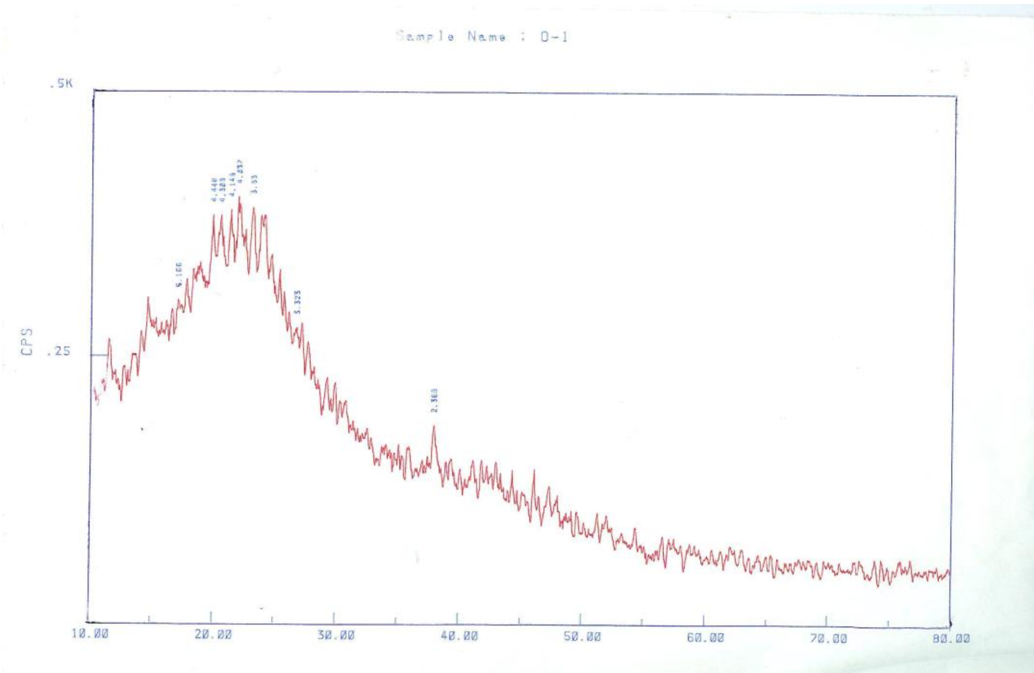


Figure 6: X-ray diffraction patterns of Char/Charcoal particles

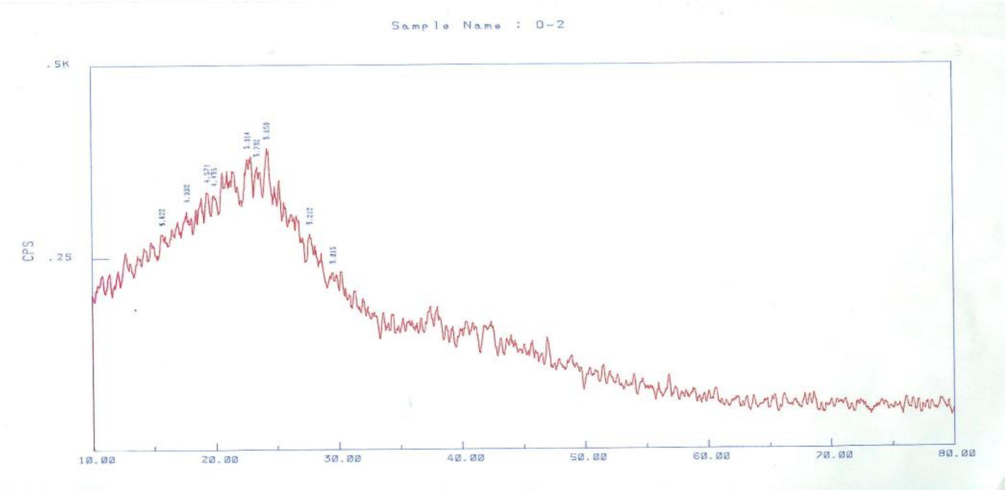


Figure 7: X-ray diffraction patterns of Char/Charcoal particles

Standard peaks (in figure) show XRD Pattern of the spring like Multi Wall Carbon Nano Fibers [31]. XRD Pattern given in Kinnow ash/char is compatible with Multi Wall Carbon Nano fibers of synthesized via mechanothermal method by Manafi, et al., [31].

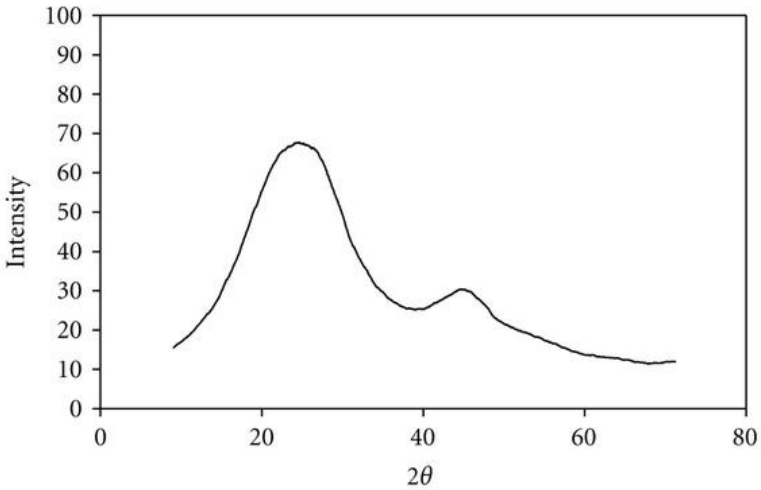


Figure 8: XRD Pattern of the spring like Multi Wall Carbon Nano Fibers.

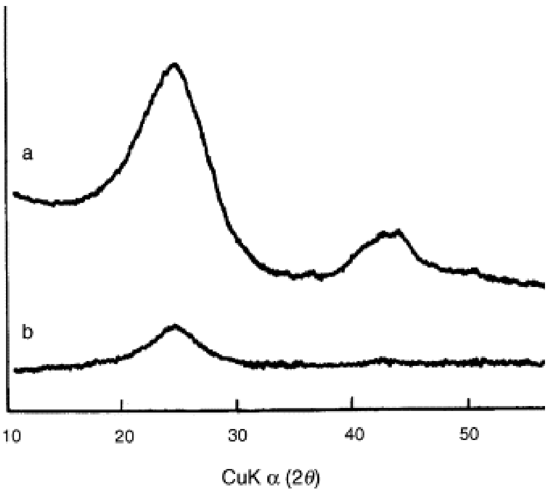


Figure 9: The XRD pattern of the carbon nano coils (a), compared to XRD pattern of carbon microcoils (b).

Standard peaks (in Figure 9) show XRD Pattern of the carbon nano coils which also confirm the formation of nano coils from Kinnow char [32].

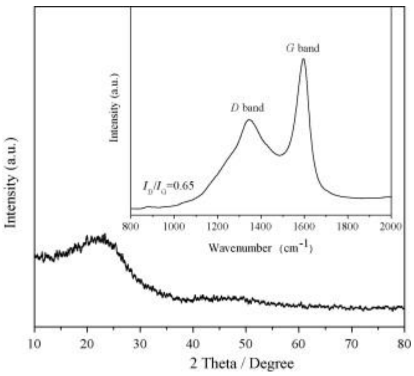
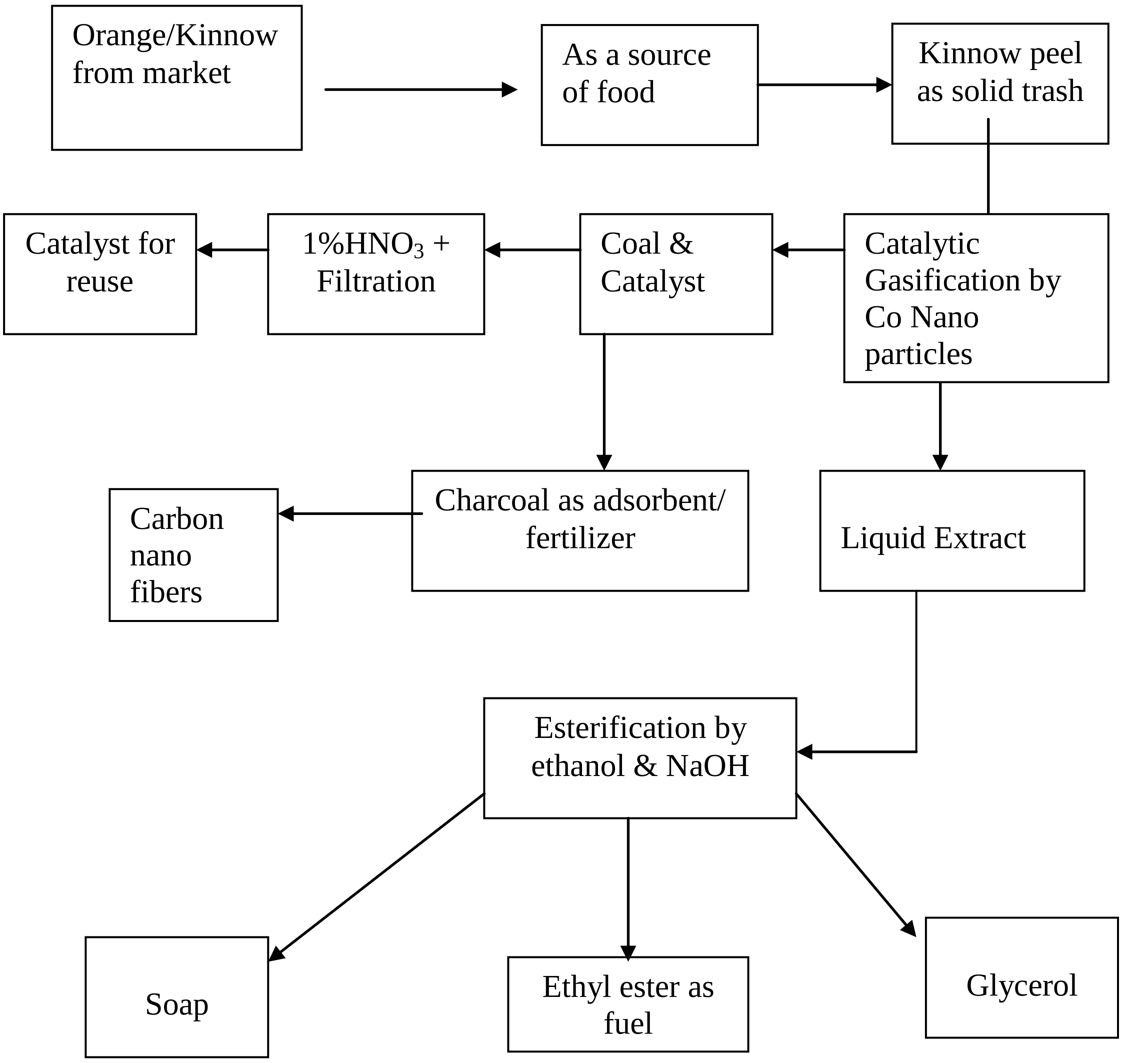


Figure 10: The XRD pattern and Raman spectrum (inset) of C_R-600

According to Du, et al., [33] a series of carbon materials [C_R-x (where x denotes carbonization temperature)] have been prepared by pyrolysis of an anion-exchange resin at 600 °C). X-ray diffraction and Raman spectroscopy suggest the presence of tiny crystalline domains in these materials, whose content is strongly determined by carbonization temperature. The XRD pattern and Raman spectrum (inset) of C_R-600 is given in Figure 10. The XRD pattern spectrum of Kinnow char is showing same pattern. So the materials may be used as light-weight and highly effective microwave absorbers over a wide frequency range. The overall process of the present study is summarized in Figure 11. This figure shows that Kinnow waste is converted into biodiesel (alkyl esters), hydrocarbon fuel gases and carbon nano tubes containing char.

Figure 11: Schematic diagram of the biofuel production from waste Kinnow peel



Conclusions

The following conclusions were drawn from this study.

1. Kinnow waste is a potential resource that can be used for cheap industrial production of biofuels.
2. Gasification waste of Kinnow peel is a best source of carbon for soil fertility and can be a source of carbon nano tubes.
3. Kinnow waste is an excellent source of environmentally friendly hydrocarbon fuel gases and alcohols.
4. The use of this solid waste as a source of biofuel will add green energy technology in the existing environment.
5. The process would be ideal for countries where Kinnow is produced and consumed.
6. This study gives a base for further research.
7. In this way solid trash may be converted into useful products in stead of dumping into

landfills.

References

2. H. de Lasa, E. Salaices, J. Mazumder, R. Lucky, Catalytic steam gasification of biomass: Thermodynamics and Kinetics, Chem. Rev., 111(2011) 5404-5433.
3. R.M. Navarro, M.C. Sanchez-Sanchez , M.C. Alvarez-Galvan, F.D. Valle, J.L.G. Ferro, Hydrogen production from renewable sources: biomass and photo catalytic opportunities, Ener. Environ. Sci., 2(2009) 35-54.
4. L. Aye, D. Yamaguchi, Supercritical water gasification of Sewage Sludge. Proceedings (526) Energy and Power System, (2006) (http://www.actapress.com/PaperInfo.aspx?paperId=23594).
5. I.K. Basily, A.L. Shafik, A.A. Sarban, M.B. Mohamed, Nanotechnology role for thr production of clean fuel E-85 and petrochemical raw materials, J. Nanotechnol., (2012) 1-5.
6. M. He, Z. Hu, J. Li, X. Guo, S. Luo, F. Yang, Y. Feng, G. Yang, S. Liu, Hydrogen-rich gas from catalytic steam gasification of municipal solid waste (MSW): Influence of catalyst and temperature on yield and product composition. Int. J. Hydrogen Ener., 34-1(2008) 195-203.
7. M. Kidwai, V. Bansal, A. Saxena, R. Shankarb, S. Mozumdar, Ni nano particles: an efficient green catalyst for chemoselective reduction of aldehydes. Tetrahedron Lett., 47(2006) 4161–4165.
8. T. Mahmood, S.T. Hussain, (2010), Nanobiotechnology for the production of biofuels from spent tea, Afri. J. Biotechnol., 9(2010) 858-868.
9. W. Yang, H. Gao, H. Xiang, D. Yin, Y. Yang, J. Yang, Y. Xu, Y. Li, Cobalt supported mesoporous silica catalyst for Fischer–Tropsch synthesis. Acta Chim. Sinica 59(2001) 1870-1877.
10. V. Kesavan, D. Dhar, Y. Koltypin, N. Perkas, O. Palchik, A. Gedanken, S. Chandrasekaran, Nano-structured amorphous metals, alloys, and metal oxides as new catalysts for oxidation, Pure Appl. Chem., 73(2001) 85–91.
11. S. Son, S. Lee, Y. Chung, S. Kim, T. Hyeon, The first intramolecular Pauson–Khand reaction in water using aqueous colloidal cobalt nano particles as catalysts, Organ. Lett., 4(2002) 277–279.
12. F. Li, Q. Liu, W. Cai, X. Shao, Analysis of scopoletin and caffeic Acid in Tobacco by GC-MS After a Rapid Derivatization Procedure. Chromatographia, 69-7(2009) 743-748.
13. H. Tsukatani, K. Tobi shi, T. Imasaka, Simple and Sensitive Determination of 2, 4-Xylenol in Surface Water Samples from River and Sea by Gas Chromatography-Mass Spectrometry. Bull. Environ. Contamin. Toxicol., 82(2009) 153–157.
14. J. Warden, L. Pereira, J. Cliff, A. Evans, GC analysis of biodiesel using a high temperature carborane modified siloxane phase column. Thermo fisher Scientific Runcorn Cheshire UK, Sundance renewable Amman ford Swansea UK. 2009.
15. M.S. Niasari, F. Davar, M. Mazaheri, M. Shaterian, Preparation of cobalt nanoparticles from [bis (salicylidene) cobalt (II)]-oleylamine complex by thermal decomposition, J. Magnetism Magnet. Mater., 320(2007) 575-578.
16. M. Guru, B.D. Artukoglu, A. Keskin, A. Koca, Biodiesel production from waste animal fat and improvement of its characteristics by synthesized nickel and magnesium additive. Energ. Convers. Manage., 50-3(2008) 498-502.
17. Y. Lin, P. Munroe, S. Joseph, S. Kimber, L.V. Zwieten, Nanoscale organo-mineral reactions of biochars in ferrosol: an investigation using microscopy, Plant and Soil, 357(2012) 369-380.
18. T. Mahmood, S.T. Hussain, S.A. Malik, New nanomaterial and the process for the production of biofuel from metal hyper accumulator water hyacinth, Afri. J Biotechnol. 9(2010) 2381-2391.
19. T. Mahmood, Metallic Phytoremediation and Nanobiotechnology of water hyacinth, PhD Thesis, Department of Biochemistry, Quid-i-Azam University Islamabad Pakistan 2011.
20. S.T. Hussain, S.A. Ali, A. Bano, T. Mahmood, Use of nanotechnology for the production of biofuels from butchery waste, Int. J. Phy. Sci, 6(2011) 7271-7279.
21. P. Quaak, H. Knoef, H. Stassen, Gasification systems, Energy from biomass- a review of combustion and gasification, World Bank Technical Paper No. 422, March 1999 energy series, Published by The World Bank, Washington D.C. 20433 U.S.A., (1999) 26-2.
23. K.R. Reddy, J.C. Tucker, Productivity and nutrient uptake of water hyacinth Eichhornia crassipes. 1. Effect of nitrogenous source. Eco. Bot. 37(1983) 237-247.
22. A. Nag, Cracking of lipids for fuels and chemicals, Biofuels refining and Performance, publisher The Mc-Graw Hill Co., Inc. New York, U.S.A., (2008) 34-35, 221-247.
24. T. Davidian, N. Guihaume, E. Iojoiu, H. Provendier, C. Mirodatos, Hydrogen production from crude pyrolysis oil by a sequential catalytic process, Appl. Catal. B: Environmental, 73(2006) 116-127.
25. T. Kimura, T. Miyazawa, J. Nishikawa, S. Kado, K. Okumura, T. Miyao, S. Naito, K. Kunimori, K. Tomishige, Development of Ni catalysts for tar removal by stream gasification of biomass, Appl. Catal. B: Environmental, 68(2006) 160-170.
26. K. Svoboda, A. Siewiorek, D. Baxter, J. Rogut, M. Pohorely, Thermodynamic possibilities and constraints for pure hydrogen production by a nickel and cobalt-based chemical looping process at lower temperatures, Enegy Conser. Manage., 49(2007) 221-231.
27. D. Swierczynski, S. Libs, C. Courson, A. Kiennemann, Steam reforming of tar from a biomass gasification process over Ni/olivine catalyst using toluene as a model compound, Appl. Catal. B: Environmental, 74(2007) 211-222.
28. G. Bran, T. Mochizuki, N. Fujishita, H. Nomoto, M. Yamada, Activation and catalytic behaviour of several Co/SiO2 catalysts for Fischer-Tropsch synthesis, Ener. Fuel, 17(2003) 799-803
29. F.R.V. Voort, A. Ghetler, D.I. Garcia-Gonzelez, Y.D. Li, Perspectives on quantitative Mid-FTIR spectroscopy in relation to edible oil and lubricant analysis : Evolution and integration of analytical methodologies, Food Anal. Meth., 1(2008) 153-163.
30. S.M. Lima, T. Izida, M.S. Figuciredo, L.H.C. Aandrade, P.V. Del-Re, N. Jorge, E. Buba, F. Aristone, Analysis of biodiesel and frying vegetable oils by means of FTIR photo acoustic spectroscopy, Eur. Phys., J. Special Topics, 153(2008) 535-537.
31. S. Manafi, M.R. Rahimipour, I. Mobasherpour, A. Soltanmoradi, The Synthesis of Peculiar Structure of Spring like Multi wall Carbon Nanofibers/Nanotubes via Mechanothermal Method, J. Nanomater. Volume 2012 (2012), Article ID 803546, 8 pages doi:10.1155/2012/803546.
32. S. Yang, X. Chen, T. Katsuno, S. Motojima, Controllable synthesis of carbon microcoils/nanocoils by catalysts supported on ceramics using catalyzed chemical vapor deposition process, Mater. Res. Bull., 42(2007) 465-473.
33. Y. Du, J. Wang, C. Cui, X. Liu, X. Wang, X. Han, Pure carbon microwave absorbers from anion-exchange resin pyrolysis, Synthetic Metals, 160(2010) 2191–2196.
34. http://www.pakissan.com/english/allabout/orchards/citrus/index.shtml

Abbreviations:

TEM = Transmission Electron Microscopy
SEM = Scanning Electron Microscopy
AFM = Atomic Force Microscopy
XPS = X-Ray Photoelectron Microscopy
XRD = X-Ray Diffraction
FTIR = Fourier Transformed Infra Red Spectroscopy
AAS = Atomic Absorption Spectroscopy
MRI = Magnetic Resonance Imaging
GC-MS = Gas Chromatography-Mass Spectrometry