MICROWAVE-ASSISTED PYROLYSIS OF CRUDE GLYCEROL

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To my beloved mother and father

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ABSTRACT

Alternative fuel very important in the renewable energy research. Crude glycerol, an excess by-product of biodiesel production that will led to environment problem was pyrolysed using a microwave heating technique under an oxygen-deficient environment over a bed of coconut shell-based activated carbon catalyst. The batch mode pyrolysis process was carried out at various temperatures and inert carrier gas flow rates to determine the yield of pyrolysis product, i.e solid (bio-char), liquid (bio-oil), and gaseous (bio-gas). The effect of catalyst on product yield was also investigated. Characterization of the pyrolysed products was performed using different instruments. Thermogravimetric analysis (TGA) was performed to determine the thermal characteristic of the bio-char. The morphology of the bio-char produced was characterised by using a field emission scanning electron (FE-SEM) and energy dispersive X-Ray (EDX). The surface area of bio-char was determined via a Brunauer, Emmett and Teller (BET) method. The functional groups of bio-oil were determined by Fourier transform infrared spectroscopy (FT-IR). A gas chromatography- mass spectormetry (GC-MS) was utilised to analyse the liquid products obtained from the experiment. Gas chromatography-thermal conductivity detector (GC-TCD) was used to analysed the bio-gas. Results shows that the increase of pyrolysis temperature led to the increase of bio-gas yield. Highest bio-gas yield was obtained for test case of 100mL/min at 700°C, while the highest bio-liquid yield was obtained for test case of 1000mL/min at 400°C. The experiment results shows that the calorific value for the liquid product was around 14.1MJ/kg and 20.6MJ/kg for gaseous product, this showed that the product that produced from the pyrolysis process had the potential to be an alternative fuels.

ABSTRAK

Bahan api alternatif merupakan kajian yang penting dalam bidang tenaga boleh baharu. Gliserol mentah merupakan hasil sampingan pengeluaran biodiesel yang terlebih dan akan menyebabkan pencemaran alam sekitar. Ia telah dipirolisis menggunakan teknik pemanasan gelombang mikro dalam persekitaran kurang oksigen dengan menggunakan pemangkin karbon aktif berasaskan kelapa. Proses pirolisis telah dijalankan pada pelbagai suhu dan kadar aliran gas lengai untuk mendapatkan hasil produk pirolisis, iaitu pepejal (bio-arang), cecair (bio-minyak), dan gas (bio-gas). Kesan pemangkin pada hasil produk itu turut disiasat. Produk yang dipirolisis dicirikan dengan menggunakan instrumen yang berbeza. Analisis termogravinetri (TGA) telah dijalankan untuk menentukan ciri haba bio-arang. Morfologi bio-arang yang dihasilkan dicirikan dengan menggunakan mikroskop imbasan elektron (FE-SEM) dan sinar-x serakan tenaga (EDX). Luas permukaan bio-char ditentukan dengan Brunauer, Emmett and Teller (BET). Kumpulan berfungsi daripada bio-minyak ditentukan dengan fourier mengubah spektrometer inframerah (FT-IR). Kromatografi gas-spektrometer jisim(GC-MS) telah digunakan untuk menganalisis produk cecair yang diperolehi daripada eksperimen. Pengesan kekonduksian terma (GC-TCD) telah digunakan untuk menganalisis bio-gas. Keputusan menunjukkan bahawa peningkatan suhu pirolisis dapat meningkatkan hasil bio-gas. Hasil bio-gas tertinggi diperoleh pada kes ujian 100ml/min pada suhu 700°C, manakala hasil paling tinggi bio-cecair yang diperoleh pada kes ujian 1000ml/min pada 400°C. Keputusan eksperimen menunjukkan bahawa nilai kalori untuk produk cecair adalah sekitar 14.1 MJ/kg dan 20.6 MJ/kg untuk produk gas. Ini menunjukkan bahawa produk yang dihasilkan daripada proses pirolisis itu berpotensi untuk menjadi bahan api alternatif

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LIST OF ABBREVIATIONS

FESEM	-	Field emission scanning electron microscope
FT-IR	-	Fourier transform infrared spectroscopy
GC-MS	-	Gas chromatography -mass spectrometry
GC-TCD	-	Gas chromatography-Thermal conductive detector
CV	-	Calorific value
AC	-	Activated carbon

LIST OF SYMBOLS

V	-	Volume of reactor
r	-	Radius
h	-	Height
Z	-	Volumetric flow rate of carrier gas
t	-	Effective residence time
x	-	Flow rate of carrier gas

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CHAPTER 1

INTRODUCTION

1.1 Background

Renewable energy is one of the main energy supply resources in the world. The limited energy resources, pollution from usage of fossil fuels and hazards of nuclear power prompt scientists to find alternative energy sources. Some potential renewable energy sources are, biomass, hydropower, geothermal, solar, wind and tidal energy. In 2013, the usage of renewable energy constituted 19.1% out of total world energy consumed, and further increased to 24.1% in year 2015 according to global status report [1-3]. The report shows that renewable energy usage is increasing in trend as a results of shift in energy policy favouring renewable energy. Figure 1.1 shows the total world energy consumption according to different sources for year (a) 2015 and (b) 2013.

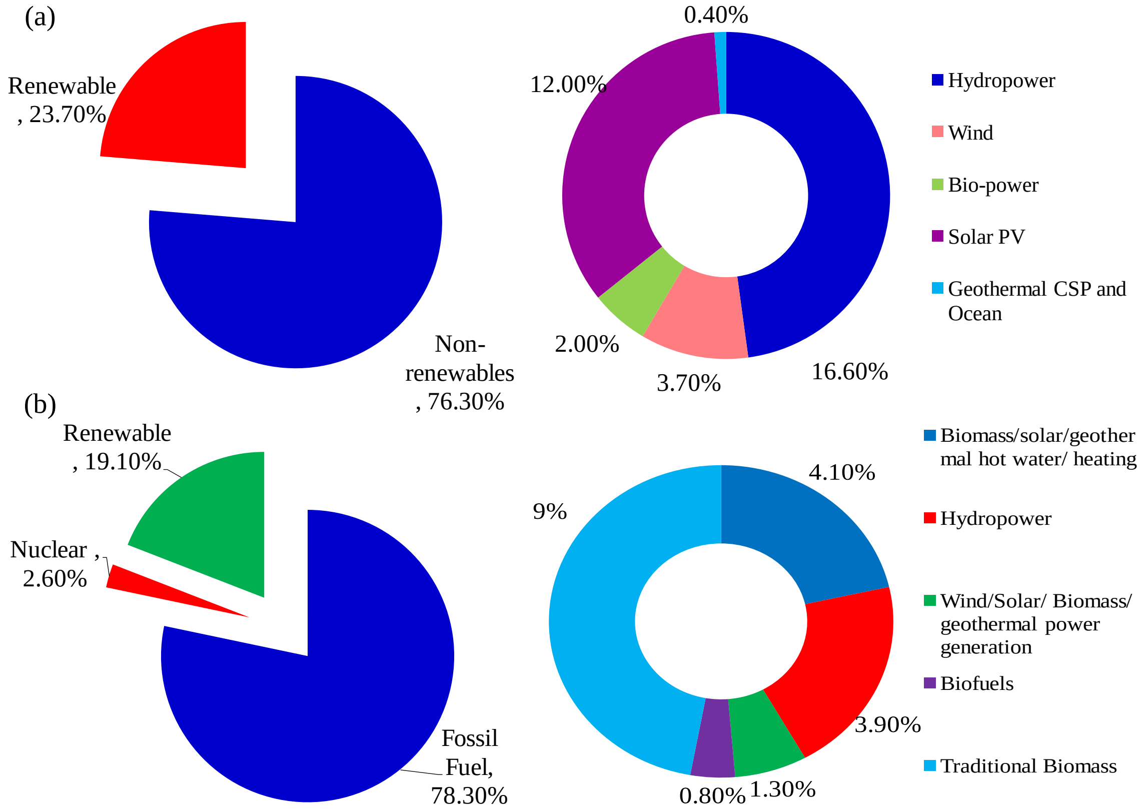
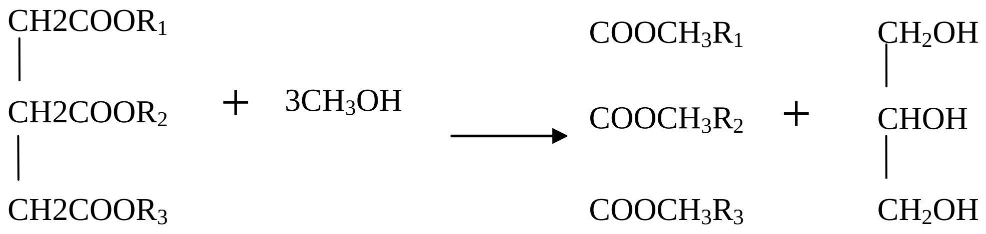


Figure 1.1: The total world energy consumption according to different source for year (a) 2015 and (b) 2013 [3].

The depleting oil reserves and pollutions from burning fossil fuels are among the problems that drive the search for alternative fuels. Biodiesel is an alternative fuel that is increasingly produced due to its clean combustion characteristic, environmental friendliness and sustainability [2]. Biodiesel is produced via transesterification process. Transesterification is the process where the triglycerides react with methanol in the presence of catalyst to produce methyl esters and by-product of glycerol as presented in Figure 1.2.



Triglycerides + Methanol ⟶ Methyl esters + Glycerine/crude glycerol
Catalyst

Figure 1.2: The chemical reaction of the transesterification process [4]**.**

Figure 1.3 shows the biodiesel and crude glycerol productions for year 2004 to 2014. The production of crude glycerol is directly related to the production of biodiesel. The increase of biodiesel production results in the corresponding increase of crude glycerol. In 2004, the annual production of biodiesel was 2.4 billion litres and increased to 29.7 billion litres at 2014, correspondingly, the global production of crude glycerol increased from 0.24 billion litres in 2004 to 2.97 billion litres in 2014 [3, 4]. The fast growing of biodiesel production and glycerol has spurred the interest to find alternative usage for crude glycerol.

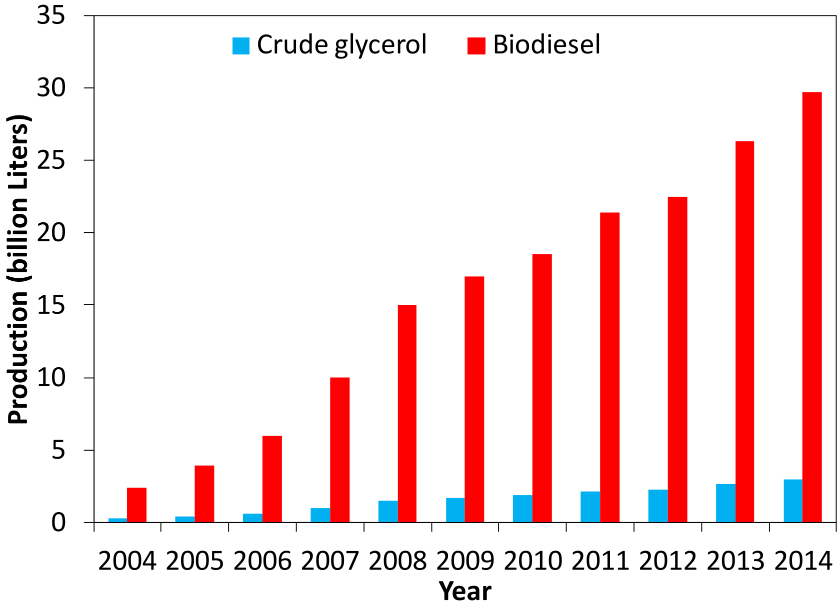


Figure 1.3: The production of biodiesel and crude glycerol for year 2004 to 2014 [3, 5, 6]

The increased supply of glycerol has resulted in the drop of crude and refined glycerols' price. Figure 1.4 shows the market price for crude and refined glycerols over the last decade. The drop in glycerol prices is directly related to the production of biodiesel. Refined glycerol is widely used in pharmaceutical, cosmetic and food industry. The price of refined glycerol is higher due to purification process involved [7]. The supply glut of crude glycerol resulted in the decrease in price for both crude and refined glycerol. It is projected that continued growth of biodiesel production will further result in the drop in glycerol price. One way to solve the problem of glycerol supply glut is to utilise crude glycerol as renewable energy by converting into bio-oil or bio-gas.

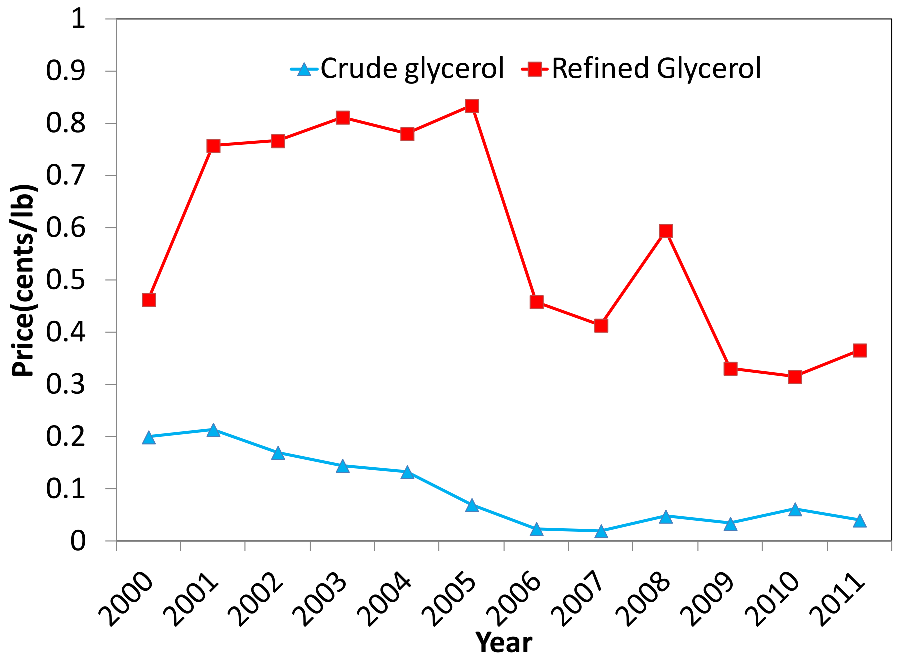


Figure 1.4: The price of crude and refined glycerol [8]

1.2 Problem Statement

With the increased production of biodiesel, an excess of glycerol is produced. The excess glycerol with low value can cause environmental problem if not properly disposed [9, 10]. Crude glycerol has high viscosity with low calorific value, thus no suitable to be used as fuel. One possible solution is to pyrolysis crude glycerol to obtain secondary products, either in gaseous or liquid fuel forms that can used as alternative fuel source. This could add value to the crude glycerol.

Pyrolysis involves thermo-chemical process. An effective way to pyrolyse crude glycerol is needed. Conventionally, direct heating using furnace could be used to pyrolyse glycerol but this method is ineffective due to high heat loss. Microwave-assisted heating is an alternative heating method that is more advantageous. However, microwave-assisted pyrolysis of crude glycerol has not been widely studied. Parametric study will be conducted to investigate the most suitable conditions for production of pyrolysis gas and liquid. Detailed characterisation of the pyrolysis product will be performed.

1.3 Objectives

The objectives of the present research is to:

- develop a microwave-assisted pyrolysis rig capable of pyrolysing liquid biomass and capturing pyrolysis product in liquid, gaseous and solid forms.
- determine the effect of carrier gas flow rate, temperature and catalyst on the pyrolysis product yield.
- characterise the crude glycerol-derived pyrolysis product, including solid, liquid and gaseous product.

1.4 Scope Of Study

The scope of the present study is to:

- Conduct literature study on the feedstock characteristic, pyrolysis, production of bio-oil, production of syngas and the method of characterising pyrolysis product.
- Develop a suitable reactor for the pyrolysis experiment. Construct a microwave pyrolysis experimental rig and select suitable catalyst for the pyrolysis experiment.
- Conduct parametric studies to determine the yield of different pyrolysis product. Subsequently, characterisation of the pyrolysis products are performed.
- Data collection, reduction and analysis.

REFERENCES1 Panwar N., Kaushik S., and Kothari S., Role of renewable energy sources in environmental protection: a review. *Renewable and Sustainable Energy Reviews*, 2011. 15(3): p. 1513-1524.

2 Leijon M., Skoglund A., Waters R., Rehn A., and Lindahl M., On the physics of power, energy and economics of renewable electric energy sources–Part I. *Renewable Energy*, 2010. 35(8): p. 1729-1734.

3 Martinot E. and Sawin J.L., Renewables 2012 global status report. *REN21 Renewable Energy Policy Network/Worldwatch Institute*, 2012. 5.

4 Yazdani S.S. and Gonzalez R., Anaerobic fermentation of glycerol: a path to economic viability for the biofuels industry. *Current opinion in biotechnology*, 2007. 18(3): p. 213-219.

5 Ren21 R., Global status report. *Renewable Energy Policy Network for the 21st Century, Paris, France*, 2010.

6 Committee R.S., Renewable 2009, Global Status Report. *World watch Institute Washington, DC*, 2009.

7 Martinot J.L.S.a.E., Global status report. *Renewable Energy Policy Network for the 21st Century, Paris, France*, 2010.

8 Quispe C.A., Coronado C.J., and Carvalho Jr J.A., Glycerol: Production, consumption, prices, characterization and new trends in combustion. *Renewable and Sustainable Energy Reviews*, 2013. 27: p. 475-493.

9 Da Silva G.P., Mack M., and Contiero J., Glycerol: a promising and abundant carbon source for industrial microbiology. *Biotechnology advances*, 2009. 27(1): p. 30-39.

10 Junior F.S.C., Cavalcante F., Alves J., and de Lima L., Parameters analysis of the assisted combustion of residual biodiesel glycerol. *International Transaction Journal of Engineering, Management, & Applied Sciences & Technologies*, 2012. 3(4): p. 10.

11 Ueoka H. and Katayama T., *Process for preparing glycerol*. 2001, Google Patents.

12 Donkin S.S., Glycerol from biodiesel production: the new corn for dairy cattle. *Revista Brasileira de Zootecnia*, 2008. 37(SPE): p. 280-286.

13 Speight J.G. and Speight J., *Chemical and process design handbook*. 2002: McGraw-Hill New York.

14 Soap and Association D., Glycerine: an overview. *Glycerine & Oleochemical Division, New York, NY*, 1990.

15 Padayachee D., Golovko V., Ingham B., and Marshall A.T., Influence of particle size on the electrocatalytic oxidation of glycerol over carbon-supported gold nanoparticles. *Electrochimica Acta*, 2014. 120: p. 398-407.

16 De Canck E., Dosuna-Rodríguez I., Gaigneaux E.M., and Van Der Voort P., Periodic mesoporous organosilica functionalized with sulfonic acid groups as acid catalyst for glycerol acetylation. *Materials*, 2013. 6(8): p. 3556-3570.

17 Devi B.P., Reddy T.V.K., Lakshmi K.V., and Prasad R., A green recyclable SO 3 H-carbon catalyst derived from glycerol for the production of biodiesel from FFA-containing karanja (Pongamia glabra) oil in a single step. *Bioresource technology*, 2014. 153: p. 370-373.

18 Bagheri S., Julkapli N.M., and Yehye W.A., Catalytic conversion of biodiesel derived raw glycerol to value added products. *Renewable and Sustainable Energy Reviews*, 2015. 41: p. 113-127.

19 Carrettin S., McMorn P., Johnston P., Griffin K., Kiely C.J., and Hutchings G.J., Oxidation of glycerol using supported Pt, Pd and Au catalysts. *Physical Chemistry Chemical Physics*, 2003. 5(6): p. 1329-1336.

20 Rodrigues E.G., Pereira M.F., Chen X., Delgado J.J., and Órfão J.J., Selective oxidation of glycerol over platinum-based catalysts supported on carbon nanotubes. *Industrial & Engineering Chemistry Research*, 2013. 52(49): p. 17390-17398.

21 Liang D., Shiyu C., Jing G., Junhua W., Ping C., and Zhaoyin H., Glycerol oxidation with oxygen over bimetallic Pt-Bi catalysts under atmospheric pressure. *Chinese Journal of Catalysis*, 2011. 32(11): p. 1831-1837.

22 Rajan N.P., Rao G.S., Pavankumar V., and Chary K.V., Vapour phase dehydration of glycerol over VPO catalyst supported on zirconium phosphate. *Catalysis Science & Technology*, 2014. 4(1): p. 81-92.

23 Yadav G.D., Sharma R.V., and Katole S.O., Selective dehydration of glycerol to acrolein: development of efficient and robust solid acid catalyst MUICaT-5. *Industrial & Engineering Chemistry Research*, 2013. 52(30): p. 10133-10144.

24 Kurosaka T., Maruyama H., Naribayashi I., and Sasaki Y., Production of 1, 3-propanediol by hydrogenolysis of glycerol catalyzed by Pt/WO 3/ZrO 2. *Catalysis Communications*, 2008. 9(6): p. 1360-1363.

25 González M.D., Salagre P., Linares M., García R., Serrano D., and Cesteros Y., Effect of hierarchical porosity and fluorination on the catalytic properties of zeolite beta for glycerol etherification. *Applied Catalysis A: General*, 2014. 473: p. 75-82.

26 Pariente S., Tanchoux N., and Fajula F., Etherification of glycerol with ethanol over solid acid catalysts. *Green Chemistry*, 2009. 11(8): p. 1256-1261.

27 Calvino-Casilda V., Guerrero-Pérez M.O., and Bañares M.A., Efficient microwave-promoted acrylonitrile sustainable synthesis from glycerol. *Green Chemistry*, 2009. 11(7): p. 939-941.

28 Dasari M.A., Kiatsimkul P.-P., Sutterlin W.R., and Suppes G.J., Low-pressure hydrogenolysis of glycerol to propylene glycol. *Applied Catalysis A: General*, 2005. 281(1): p. 225-231.

29 Gomes J.F., Gasparotto L.H., and Tremiliosi-Filho G., Glycerol electro-oxidation over glassy-carbon-supported Au nanoparticles: direct influence of the carbon support on the electrode catalytic activity. *Physical Chemistry Chemical Physics*, 2013. 15(25): p. 10339-10349.

30 Miranda B., Chimentao R.J., Santos J.B., Gispert-Guirado F., Llorca J., Medina F., Bonillo F.L., and Sueiras J.E., Conversion of glycerol over 10% Ni/γ-Al 2 O 3 catalyst. *Applied Catalysis B: Environmental*, 2014. 147: p. 464-480.

31 Lehr V., Sarlea M., Ott L., and Vogel H., Catalytic dehydration of biomass-derived polyols in sub-and supercritical water. *Catalysis Today*, 2007. 121(1): p. 121-129.

32 Maglinao R.L. and He B.B., Catalytic thermochemical conversion of glycerol to simple and polyhydric alcohols using raney nickel catalyst. *Industrial & Engineering Chemistry Research*, 2011. 50(10): p. 6028-6033.

33 Bühler W., Dinjus E., Ederer H., Kruse A., and Mas C., Ionic reactions and pyrolysis of glycerol as competing reaction pathways in near-and supercritical water. *The Journal of Supercritical Fluids*, 2002. 22(1): p. 37-53.

34 Wu Z., Mao Y., Wang X., and Zhang M., Preparation of a Cu–Ru/carbon nanotube catalyst for hydrogenolysis of glycerol to 1, 2-propanediol via hydrogen spillover. *Green Chemistry*, 2011. 13(5): p. 1311-1316.

35 Furikado I., Miyazawa T., Koso S., Shimao A., Kunimori K., and Tomishige K., Catalytic performance of Rh/SiO 2 in glycerol reaction under hydrogen. *Green chemistry*, 2007. 9(6): p. 582-588.

36 Yin C., Microwave-assisted pyrolysis of biomass for liquid biofuels production. *Bioresource technology*, 2012. 120: p. 273-284.

37 Fernández Y., Arenillas A., and Menéndez J.Á., *Microwave heating applied to pyrolysis*. 2011: InTech.

38 Motasemi F. and Afzal M.T., A review on the microwave-assisted pyrolysis technique. *Renewable and Sustainable Energy Reviews*, 2013. 28: p. 317-330.

39 Lam S.S., Liew R.K., Jusoh A., Chong C.T., Ani F.N., and Chase H.A., Progress in waste oil to sustainable energy, with emphasis on pyrolysis techniques. *Renewable and Sustainable Energy Reviews*, 2016. 53: p. 741-753.

40 Domínguez A., Fernández Y., Fidalgo B., Pis J., and Menéndez J., Bio-syngas production with low concentrations of CO 2 and CH 4 from microwave-induced pyrolysis of wet and dried sewage sludge. *Chemosphere*, 2008. 70(3): p. 397-403.

41 Menéndez J., Domínguez A., Fernández Y., and Pis J., Evidence of self-gasification during the microwave-induced pyrolysis of coffee hulls. *Energy & Fuels*, 2007. 21(1): p. 373-378.

42 Zhao X., Song Z., Liu H., Li Z., Li L., and Ma C., Microwave pyrolysis of corn stalk bale: A promising method for direct utilization of large-sized biomass and syngas production. *Journal of Analytical and Applied Pyrolysis*, 2010. 89(1): p. 87-94.

43 Mullen C.A., Boateng A.A., Goldberg N.M., Lima I.M., Laird D.A., and Hicks K.B., Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis. *Biomass and bioenergy*, 2010. 34(1): p. 67-74.

44 Imam T. and Capareda S., Characterization of bio-oil, syn-gas and bio-char from switchgrass pyrolysis at various temperatures. *Journal of Analytical and Applied Pyrolysis*, 2012. 93: p. 170-177.

45 Solantausta Y., Nylund N.-O., Westerholm M., Koljonen T., and Oasmaa A., Wood-pyrolysis oil as fuel in a diesel-power plant. *Bioresource Technology*, 1993. 46(1): p. 177-188.

46 Gust S., *Combustion experiences of flash pyrolysis fuel in intermediate size boilers*, in *Developments in thermochemical biomass conversion*. 1997, Springer. p. 481-488.

47 Demirbaş A., Partly chemical analysis of liquid fraction of flash pyrolysis products from biomass in the presence of sodium carbonate. *Energy conversion and management*, 2002. 43(14): p. 1801-1809.

48 Xie Q., Peng P., Liu S., Min M., Cheng Y., Wan Y., Li Y., Lin X., Liu Y., and Chen P., Fast microwave-assisted catalytic pyrolysis of sewage sludge for bio-oil production. *Bioresource technology*, 2014. 172: p. 162-168.

49 Menéndez J., Domınguez A., Inguanzo M., and Pis J., Microwave pyrolysis of sewage sludge: analysis of the gas fraction. *Journal of Analytical and Applied Pyrolysis*, 2004. 71(2): p. 657-667.

50 Zhao X., Wang M., Liu H., Zhao C., Ma C., and Song Z., Effect of temperature and additives on the yields of products and microwave pyrolysis

behaviors of wheat straw. *Journal of Analytical and Applied Pyrolysis*, 2013. 100: p. 49-55.

51 Al Shra'ah A. and Helleur R., Microwave pyrolysis of cellulose at low temperature. *Journal of Analytical and Applied Pyrolysis*, 2014. 105: p. 91-99.

52 Salema A.A. and Ani F.N., Microwave induced pyrolysis of oil palm biomass. *Bioresource Technology*, 2011. 102(3): p. 3388-3395.

53 Khaghanikavkani E., Farid M.M., Holdem J., and Williamson A., Microwave pyrolysis of plastic. *Journal of Chemical Engineering & Process Technology*, 2013. 2013.

54 Beneroso D., Bermúdez J., Arenillas A., and Menéndez J., Influence of carrier gas on microwave-induced pyrolysis. *Journal of Analytical and Applied Pyrolysis*, 2015. 113: p. 153-157.

55 Lima D.G., Soares V.C., Ribeiro E.B., Carvalho D.A., Cardoso É.C., Rassi F.C., Mundim K.C., Rubim J.C., and Suarez P.A., Diesel-like fuel obtained by pyrolysis of vegetable oils. *Journal of Analytical and Applied Pyrolysis*, 2004. 71(2): p. 987-996.

56 Fernández Y., Arenillas A., Díez M., Pis J., and Menéndez J., Pyrolysis of glycerol over activated carbons for syngas production. *Journal of Analytical and Applied Pyrolysis*, 2009. 84(2): p. 145-150.

57 Valliyappan T., Bakhshi N., and Dalai A., Pyrolysis of glycerol for the production of hydrogen or syn gas. *Bioresource Technology*, 2008. 99(10): p. 4476-4483.

58 Ganesapillai M., Manara P., and Zabaniotou A., Effect of microwave pretreatment on pyrolysis of crude glycerol–olive kernel alternative fuels. *Energy Conversion and Management*, 2016. 110: p. 287-295.

59 Tamošiūnas A., Valatkevičius P., Grigaitienė V., Valinčius V., and Striūgas N., A cleaner production of synthesis gas from glycerol using thermal water steam plasma. *Journal of Cleaner Production*, 2015.

60 Soares R.R., Martins D.F., Pereira D.E., Almeida M.B., and Lam Y.L., On the gas-phase reforming of glycerol by Pt on carbon black: Effects of metal particle size and pH value of the glycerol stream. *Journal of Molecular Catalysis A: Chemical*, 2016.

61 Liu J., Takada R., Karita S., Watanabe T., Honda Y., and Watanabe T., Microwave-assisted pretreatment of recalcitrant softwood in aqueous glycerol. *Bioresource technology*, 2010. 101(23): p. 9355-9360.

62 Dalil M., Edake M., Sudeau C., Dubois J.-L., and Patience G.S., Coke promoters improve acrolein selectivity in the gas-phase dehydration of glycerol to acrolein. *Applied Catalysis A: General*, 2016. 522: p. 80-89.

63 dos Santos M.B., Andrade H.M., and Mascarenhas A.J., Reduced coke formation during the gas phase oxidative dehydration of glycerol over ferrierite zeolites synthesized in fluoride medium. *Microporous and Mesoporous Materials*, 2016. 223: p. 105-113.

64 Peres A., de Lima D., da Silval N.d.L., and Maciel M.W., Syngas production and optimization from glycerol pyrolysis. *CHEMICAL ENGINEERING*, 2010. 20.

65 Adhikari S., Fernando S.D., and Haryanto A., Hydrogen production from glycerin by steam reforming over nickel catalysts. *Renewable energy*, 2008. 33(5): p. 1097-1100.

66 Sánchez E.A., D'Angelo M.A., and Comelli R.A., Hydrogen production from glycerol on Ni/Al 2 O 3 catalyst. *International Journal of Hydrogen Energy*, 2010. 35(11): p. 5902-5907.

67 Iriondo A., Cambra J., Güemez M., Barrio V., Requies J., Sánchez-Sánchez M., and Navarro R., Effect of ZrO 2 addition on Ni/Al 2 O 3 catalyst to produce H 2 from glycerol. *international Journal of Hydrogen Energy*, 2012. 37(8): p. 7084-7093.

68 Dou B., Dupont V., Rickett G., Blakeman N., Williams P.T., Chen H., Ding Y., and Ghadiri M., Hydrogen production by sorption-enhanced steam reforming of glycerol. *Bioresource Technology*, 2009. 100(14): p. 3540-3547.

69 Liu S.-K. and Lin Y.-C., Autothermal partial oxidation of glycerol to syngas over Pt-, LaMnO3-, and Pt/LaMnO3-coated monoliths. *Industrial & Engineering Chemistry Research*, 2012. 51(50): p. 16278-16287.

70 Lin K.-H., Chang A.C.-C., Lin W.-H., Chen S.-H., Chang C.-Y., and Chang H.-F., Autothermal steam reforming of glycerol for hydrogen production over packed-bed and Pd/Ag alloy membrane reactors. *International Journal of Hydrogen Energy*, 2013. 38(29): p. 12946-12952.

71 Dauenhauer P., Salge J., and Schmidt L., Renewable hydrogen by autothermal steam reforming of volatile carbohydrates. *Journal of Catalysis*, 2006. 244(2): p. 238-247.

72 Swami S.M. and Abraham M.A., Integrated catalytic process for conversion of biomass to hydrogen. *Energy & fuels*, 2006. 20(6): p. 2616-2622.

73 Guo Y., Azmat M.U., Liu X., Wang Y., and Lu G., Effect of support’s basic properties on hydrogen production in aqueous-phase reforming of glycerol and correlation between WGS and APR. *Applied Energy*, 2012. 92: p. 218-223.

74 Tuza P.V., Manfro R.L., Ribeiro N.F., and Souza M.M., Production of renewable hydrogen by aqueous-phase reforming of glycerol over Ni–Cu catalysts derived from hydrotalcite precursors. *Renewable Energy*, 2013. 50: p. 408-414.

75 Wen G., Xu Y., Ma H., Xu Z., and Tian Z., Production of hydrogen by aqueous-phase reforming of glycerol. *International Journal of Hydrogen Energy*, 2008. 33(22): p. 6657-6666.

76 Pairojpiriyakul T., Croiset E., Kiatkittipong W., Kiatkittipong K., Arpornwichanop A., and Assabumrungrat S., Hydrogen production from catalytic supercritical water reforming of glycerol with cobalt-based catalysts. *International Journal of Hydrogen Energy*, 2013. 38(11): p. 4368-4379.

77 Pairojpiriyakul T., Kiatkittipong W., Assabumrungrat S., and Croiset E., Hydrogen production from supercritical water reforming of glycerol in an empty Inconel 625 reactor. *International Journal of Hydrogen Energy*, 2014. 39(1): p. 159-170.

78 Xu D., Wang S., Hu X., Chen C., Zhang Q., and Gong Y., Catalytic gasification of glycine and glycerol in supercritical water. *International Journal of Hydrogen Energy*, 2009. 34(13): p. 5357-5364.

79 Ortiz F.G., Campanario F., Aguilera P., and Ollero P., Supercritical water reforming of glycerol: Performance of Ru and Ni catalysts on Al 2 O 3 support. *Energy*, 2016. 96: p. 561-568.

80 Schwengber C.A., Alves H.J., Schaffner R.A., da Silva F.A., Sequinel R., Bach V.R., and Ferracin R.J., Overview of glycerol reforming for hydrogen

production. *Renewable and Sustainable Energy Reviews*, 2016. 58: p. 259-266.

81 Lam S.S., Russell A.D., Lee C.L., and Chase H.A., Microwave-heated pyrolysis of waste automotive engine oil: Influence of operation parameters on the yield, composition, and fuel properties of pyrolysis oil. *Fuel*, 2012. 92(1): p. 327-339.

82 Huang Y., Kuan W., Lo S., and Lin C., Hydrogen-rich fuel gas from rice straw via microwave-induced pyrolysis. *Bioresource technology*, 2010. 101(6): p. 1968-1973.

83 Ringer M., Putsche V., and Scahil J., *Large-Scale Pyrolysis Oil Production: A Technology Assessment and Economic Analysis. Golden (CO): National Renewable Energy Laboratory; 2006 Nov. Report No*. 2006, NREL/TP-510-37779. Contract No.: DE-AC36-99-GO10337.

84 Valliyappan T., *Hydrogen or syn gas production from glycerol using pyrolysis and steam gasification processes*. 2004, University of Saskatchewan Saskatoon.

85 Ningbo G., Baoling L., Aimin L., and Juanjuan L., Continuous pyrolysis of pine sawdust at different pyrolysis temperatures and solid residence times. *Journal of Analytical and Applied Pyrolysis*, 2015. 114: p. 155-162.

86 Özçimen D. and Ersoy-Meriçboyu A., A study on the carbonization of grapeseed and chestnut shell. *Fuel Processing Technology*, 2008. 89(11): p. 1041-1046.

87 Scott D.S., Piskorz J., Bergougnou M.A., Graham R., and Overend R.P., The role of temperature in the fast pyrolysis of cellulose and wood. *Industrial & engineering chemistry research*, 1988. 27(1): p. 8-15.

88 Zabaniotou A., Kalogiannis G., Kappas E., and Karabelas A., Olive residues (cuttings and kernels) rapid pyrolysis product yields and kinetics. *Biomass and bioenergy*, 2000. 18(5): p. 411-420.

89 Heo H.S., Park H.J., Park Y.-K., Ryu C., Suh D.J., Suh Y.-W., Yim J.-H., and Kim S.-S., Bio-oil production from fast pyrolysis of waste furniture sawdust in a fluidized bed. *Bioresource technology*, 2010. 101(1): p. S91-S96.

90 Ningbo G., Baoling L., Aimin L., and Juanjuan L., Continuous pyrolysis of pine sawdust at different pyrolysis temperatures and solid residence times. *Journal of Analytical and Applied Pyrolysis*, 2015.

91 Menéndez J., Arenillas A., Fidalgo B., Fernández Y., Zubizarreta L., Calvo E., and Bermúdez J., Microwave heating processes involving carbon materials. *Fuel Processing Technology*, 2010. 91(1): p. 1-8.

92 A. Domínguez J.A.M., M. Inguanzo, P.L. Bernard, J.J. Pis, Gas chromatographic–mass spectrometric study of the oil fractions produced by microwave-assisted pyrolysis of different sewage sludges. *Journal of Chromatography A*, 2003. 1012(2): p. 193-206.

93 Wang J., Zhang M., Chen M., Min F., Zhang S., Ren Z., and Yan Y., Catalytic effects of six inorganic compounds on pyrolysis of three kinds of biomass. *Thermochimica acta*, 2006. 444(1): p. 110-114.

94 Schmidt H.-P., 55 uses of biochar. *Journal for ecology, winegrowing and climate farming, posted on December*, 2012. 29.

95 Apaydın-Varol E. and Pütün A.E., Preparation and characterization of pyrolytic chars from different biomass samples. *Journal of Analytical and Applied Pyrolysis*, 2012. 98: p. 29-36.

96 Özçimen D. and Ersoy-Meriçboyu A., Characterization of biochar and bio-oil samples obtained from carbonization of various biomass materials. *Renewable Energy*, 2010. 35(6): p. 1319-1324.

97 Haykırı-Açma H., Ersoy-Meriçboyu A., and Küçükbayrak S., Effect of mineral matter on the reactivity of lignite chars. *Energy conversion and management*, 2001. 42(1): p. 11-20.

98 Uzun B.B., Apaydin-Varol E., Ateş F., Özbay N., and Pütün A.E., Synthetic fuel production from tea waste: Characterisation of bio-oil and bio-char. *Fuel*, 2010. 89(1): p. 176-184.

99 Demiral I. and Kul Ş.Ç., Pyrolysis of apricot kernel shell in a fixed-bed reactor: characterization of bio-oil and char. *Journal of Analytical and Applied Pyrolysis*, 2014. 107: p. 17-24.

100 Ahn S.Y., Eom S.Y., Rhie Y.H., Sung Y.M., Moon C.E., Choi G.M., and Kim D.J., Utilization of wood biomass char in a direct carbon fuel cell (DCFC) system. *Applied Energy*, 2013. 105: p. 207-216.

101 Adamson A.W. and Gast A.P., Physical chemistry of surfaces. 1967.

102 Abdel-Fattah T.M., Mahmoud M.E., Ahmed S.B., Huff M.D., Lee J.W., and Kumar S., Biochar from woody biomass for removing metal contaminants and carbon sequestration. *Journal of Industrial and Engineering Chemistry*, 2015. 22: p. 103-109.

103 Angın D., Effect of pyrolysis temperature and heating rate on biochar obtained from pyrolysis of safflower seed press cake. *Bioresource technology*, 2013. 128: p. 593-597.

104 Yagmur E., Ozmak M., and Aktas Z., A novel method for production of activated carbon from waste tea by chemical activation with microwave energy. *Fuel*, 2008. 87(15): p. 3278-3285.

105 Kirubakaran V., Sivaramakrishnan V., Nalini R., Sekar T., Premalatha M., and Subramanian P., A review on gasification of biomass. *Renewable and Sustainable Energy Reviews*, 2009. 13(1): p. 179-186.

106 Donahue C.J. and Rais E.A., Proximate analysis of coal. *Journal of Chemical Education*, 2009. 86(2): p. 222.

107 Vaimakis T.C., Thermogravimetry (TG) or Thermogravimetric Analysis (TGA).

108 Lambert J., Shurvell H., Lightner D., and Cooks R., Organic Structural SpectroscopyPrentice Hall. *Englewood Cliffs, NJ*, 1998: p. 31.

109 Zhou L., Yang H., Wu H., Wang M., and Cheng D., Catalytic pyrolysis of rice husk by mixing with zinc oxide: characterization of bio-oil and its rheological behavior. *Fuel Processing Technology*, 2013. 106: p. 385-391.

110 Onay O. and Koçkar O.M., Fixed-bed pyrolysis of rapeseed (Brassica napus L.). *Biomass and Bioenergy*, 2004. 26(3): p. 289-299.

111 Bhattacharya P., Steele P.H., El Barbary M.H., Mitchell B., Ingram L., and Pittman C.U., Wood/plastic copyrolysis in an auger reactor: Chemical and physical analysis of the products. *Fuel*, 2009. 88(7): p. 1251-1260.

112 Wang D., Montane D., and Chornet E., Catalytic steam reforming of biomass-derived oxygenates: acetic acid and hydroxyacetaldehyde. *Applied Catalysis A: General*, 1996. 143(2): p. 245-270.

113 Avasthi K.S., Reddy R.N., and Patel S., Challenges in the production of hydrogen from glycerol–a biodiesel byproduct via steam reforming process. *Procedia Engineering*, 2013. 51: p. 423-429.

114 Chen H., Ding Y., Cong N.T., Dou B., Dupont V., Ghadiri M., and Williams P.T., A comparative study on hydrogen production from steam-glycerol reforming: thermodynamics and experimental. *Renewable Energy*, 2011. 36(2): p. 779-788.