Co-pyrolysis of Rice Husk with Underutilized Biomass Species: A Sustainable Route for Production of Precursors for Fuels and Valuable Chemicals

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Abstract

In this study, co-pyrolysis of rice husk with underutilized biomass, Napier grass and sago waste was carried out in a fixed bed reactor at 600 ^{o}C, 30 ^{o}C/min and 5L/min nitrogen flowrate. Two-phase bio-oil (organic and aqueous) was collected and characterized using standard analytical techniques. 34.13-45.55 wt % total boil-oil yield was recorded using assorted biomass compared to pure risk husk biomass with 31.51 wt% yield. The organic phase consist mainly benzene derivatives with higher proportion in the oil from the co-pyrolysis process relative to the organic phase from the pyrolysis of the individual biomass while the aqueous phase in all cases was predominantly water, acids, ketones, aldehydes, sugars and traces of phenolics. This study has demonstrated a good approach towards increasing valorization of rice husk in a single reaction step for the production of high grade bio-oil, which can be transformed into fuel and valuable chemicals.

Keywords: Rice husk; Napier grass; Sago waste; Co-pyrolysis; Bio-oil; Characterization

1. Introduction

Emission of greenhouse gases (GHG) from the use of fossil fuel continues to generate serious concerns due to its negative impacts on the climate change[1-4]. Only recently, the United Nations conference on climate change held in Paris November 2015 with the participants from over 180 countries set a target to limit the global temperature rise to below 2 ^{o}C [1]. To achieve this, a drastic reduction in energy contribution from fossil fuel and development of more alternative and sustainable energy sources is needed in order to maintain energy security. Lignocellulosic biomass (forest residues, agro-wastes, energy grasses, aquatic plants, algae, etc.), which are non-food materials remains one of the renewable energy sources with high prospects to be transformed into fuel, valuable chemicals and other value added bio-products. Rice husk (RH) is one of the most common agro-residue in rice producing countries such as Malaysia, China, Thailand, Indonesia, India, etc. In 2013, rice production in Malaysia increased to about 2.6 million tonnes which generated around 703 tonnes RH [2]. This agro-waste posed a serious solid waste disposal since the traditional method of disposal (open burning) is no longer accepted as it leads to emissions which is another environmental challenge. Currently, rice husk is being used as a raw material for production of bioenergy and valuable materials via thermochemical and biochemical processes [3-6]. Pyrolysis is a thermochemical process where biomass materials can be converted into solid (bio-char), liquid (bio-oil) and gaseous products (non-condensable) under inert environment. This process continues to be attractive as it comprises fewer steps, relatively less complex and virtually all kinds of biomass material can be processed. High bio-oil yield up to 75% can be obtained under a careful control of process parameters [7-9]. Studies on pyrolysis of RH to bio-oil have been carried out by many researchers [10-21]. Bio-oil yields between 25 and 38 wt% rich in acid and ketones are mostly recorded during the pyrolysis of RH at around 600 ^{o}C [12, 13, 16, 18-21]. Catalytic pyrolysis is also being used towards improving

the oil quality from RH, and a considerable degree of deoxygenation is achieved at the detriment of oil yield [20-22]. This process is normally conducted through in-bed mixing, having biomass and catalyst in the same reactor or the use of multiple reactors with materilas in separate compartment[19-23]. In the former, utilization of all pyrolysis products for energy production may not be possible. Bio-char from this process contain spent catalysts which are usually difficult to separate. Using such bio-char could result to emission of poisonous particulate matters since most catalysts are made up of metals which are not combustible and environmentally friendly. On the other hand, multiple reactor system could be highly energy intensive as both reactors need to be maintained at high temperatures.

Underutilized or neglected biomass here refers to materials from non-food crops or residues from food crops with unrealised potentials. Typical examples of the underutilized biomass include Napier grass, residues from Sweet sorghum, Millet, Nipa, Sago, Bambara groundnut, Leucaena, etc. Using these materials for bioenergy production will not only increase energy security but also food security. Land, water and other productive resources that would have been used for cultivation of dedicated energy or oil crops such as Jatropha, mustard etc will be geared towards the cultivation of the food crops. This approach can therefore be said to be a sustainable way of reducing GHGs since the residuals from the underutilized crops can render the use of fossil fuels unnecessary. In addition, it will also increase agricultural sustainability through reduction in inputs, such as fossil fuel-derived fuel and nitrogen fertilizers.

Co-pyrolysis is similar to the traditional pyrolysis process, but more than one material is used as a feedstock. This process has been identified as an efficient technique for improving the quantity and quality of the product bio-oil produced in a single step reaction. Successes of this technique have been linked to the synergistic effect resulting from the reaction of different components and

radicals during the pyrolysis [24]. Co-pyrolysis of lignocellulosic biomass with other materials such as coal, waste plastics, tyres, sludge, papers, oils, etc have been reported in the literature [24-29]. The results of these findings revealed that the product bio-oil had improved chemical and physicochemical properties. To the best of our knowledge, co-pyrolysis of RH with underutilized biomass has not been reported in the literature. The objective of this study was study the synergism between RH and Napier grass (NG), sago waste (SGW) and the impact on yield and quality of resulting bio-oil.

2. Materials and method

All the biomass materials used in this study were obtained locally in Malaysia. Paddy RH, Napier grass stem (NG) and sago biomass (SGW) was collected from a rice processing mill Sungai Besar, Selangor, Crop for the Future research Centre Semenyih Selangor and sago flour process plant effluent Pusa Sarawak respectively. Proximate and ultimate analyses were performed according to standard analytical methods [30]. The feedstock composition used was varied according to the scenario summarized in Table 1. Thermogravimetric study was carried out in thermogravimetric simultaneous thermal analyzer (STA) 6000 (TGA) (Perkin Elmer Sdn Bhd, Selangor, Malaysia) in a nitrogen atmosphere, flow rate 20mL/min at temperatures between 300-1050 K and heating rate of 10 K/min. About 10.0 mg (particle size of 0.2 mm) of sample was used. Intermediate pyrolysis was conducted in a horizontal fixed bed reactor at 600 ^{o}C, 30 ^{o}C/min and 5 L/min nitrogen flowrate as shown in Figure 1. The unit consists of a stainless tube reactor (115 cm length, 5 cm inner diameter), oil collector, gas scrubbers and water chiller operating at 3 ^{o}C attached to a coil condenser. The feedstock (100 g bone dry, 0.2-2 mm particle size) was placed at center of the reactor and heated electrically under nitrogen atmosphere. Actual pyrolysis temperature was monitored with a K-type thermocouple connected to computer

through a data logger. The reaction time was kept at 60 min (±2 min) after the reaction temperature reaches 600 ^{o}C. Bio-oil, bio-char and non-condensable yields were determined according to equation 1, 2 and 3 respectively. Bio-oil collected was characterized. The water content in the bio-oil was determined using Karl Fischer V20 volumetric titrator (Mettler Toledo, USA) [31, 32]. Higher heating value was determined using an oxygen bomb calorimeter (Parr 6100) [32-33]. Elemental compositions of the oil was determined using Perkin Elmer 2400 Series II CHNS/O analyzer (Perkin Elmer Sdn Bhd, Selangor, Malaysia). Detail of the chemical composition of the bio-oil was analysed using a gas chromatograph-mass spectrometer (GC-MS) system (PerkinElmer Clarus^R SQ 8, USA) with a quadruple detector and PerkinElmer-Elite^{TM}-5ms column (30m x 0.25mm x 0.25µm). Peaks of the chromatogram were identified by comparing with standard spectra of compounds in the National Institute of Standards and Technology (NIST) library. Each experiment was repeated three times and average value and standard deviations (SD) were computed.

3. Results and discussion

3.1 Characterization of feedstock

Characteristics of the individual and assorted biomass are summarized in Table 2. From the proximate analysis, comparing scenario 1, 2 and 3 (pure NG, RH and SGW), it can be seen that scenario 2 recorded highest ash content and lower volatile matter. With respect to scenario 4, 5 and 6 (assorted biomass), substantial reduction in the ash content, particularly in the case 4 and6, and improvement in the volatile matter were recorded. Ultimate analysis revealed that case 2 had lowest carbon and highest oxygen contents. This together with the proximate properties may be responsible for the lower energy content recorded. The result of TGA analysis of case study 1, 2 and 3 is shown in Figure 2. From the DTG curve, NG (case 1) exhibited three peaks around 460,

545 and 585K which is attributed to the degradation of extractives, hemicellulose and cellulose respectively. RH showed two peaks around 560 and 610 K which is ascribed to hemicellulose and cellulose decomposition. This observation suggests that RH (case 2) has lesss or infinitesimal amount of extractives and its degradation aligned with that of hemicellulose. For SGW (case 3), only the cellulose decomposition peak around 592K was observed due to high amount of holocellulose present in it [34]. Characteristics of all the samples were similar in the lignin decomposition region around 610 K and above. No noticeable peak was observed due to low thermal decomposition characteristic of lignin which spans over a wide temperature range. The major inorganic element in the ash such as potassium (K), calcium (Ca) and silicon (Si) determined using atomic absorption spectrometer (AAS) Perkin Elmer analyst 400 (Perkin Elmer Sdn Bhd, Selangor, Malaysia) according to BS EN 15290 are summarized in the table 3. The result revealed that proportion of the elements in the ash are in the following order K>Ca>Si, Si>K>Ca and Ca>Si>K for the case study 1, 2 and 3 (pure biomass samples) respectively while Si>K>Ca was recorded for the remaining case studies (assorted biomass samples).

3.2   Pyrolysis product distribution and physicochemical properties of the bio-oil

The pyrolysis product distribution is shown in Figure 3. The total bio-oil (organic and aqueous) yield recorded from pure RH (case study 2) was 31.51 wt% (30.70-aqueous, 0.82-organic) which is comparable with the literature values [12, 11, 15, 17-20] while 41.91 wt% (29.56-aqueous, 12.34-organic) and 37.98 wt% (36.87-aqueous, 1.11-organic) was recorded for pure NG (case study 1) and SGW (case study 2) respectively. On the other hand, the assorted biomass recorded total bio-oil yield of 35.86 wt% (32.66-aqueous, 1.11-organic), 45.55 wt% (36.60-aqueous, 8.95-organic) and 34.13 wt% (31.98-aqueous, 2.14-organic) for the case 4, 5 and 6 correspondingly. The higher bio-oil yield recorded during the co-pyrolysis relative to the oil observed in case 2

can be related to the characteristic of the biomass feed, particularly the biomass ash and its composition. This also confirms the existence of synergistic effect during the co-pyrolysis. Figure 4 showed a correlation between the total bio-oil yield and the ash content in the feedstock. Bio-oil yield decreased with increasing ash content. High ash content biomass generally produce more solid materials since ash is non-combustible and therefore will remain in the solid product after the pyrolysis [34, 35]. The bio-oil aqueous phase, which is normally made up of sugars, acids, ketones and aldehyde showed a direct connection with the ash content of the feedstock (Figure 3). This could be due to the nature of mineral elements in the ash, particularly the alkaline and alkaline earth metals. These elements tend to catalyze pyrolysis reactions which usually lead to degradation and polymerization of the intermediate products [36, 37]. Studies have shown that the addition of alkaline earth metal (Ca) promotes the formation of liquid product during pyrolysis [38, 39] and therefore, the increased aqueous phase bio-oil observed in this study can be attributed to catalytic activity of the Ca mineral in the ash (table 3). The yield of bio-char observed is attributed to the combined effect of K and Si in the ash. The bio-char yield (Figure 2) increased with increasing resultant minerals (K and Si) (table 3), especially for the case of the assorted biomass feedstock. This observation is in good agreement with the work of Wang *et al* [38] where it was established that addition of potassium (K) compound to pine biomass increased the char yield during pyrolysis. For the yield of non-condensable gas, slight changes were recorded in the all the case studies except the case study 3 (pure SGW) (Figure 2) where the highest non-condensable gas was recorded. This observation is attributed to the high amount oxygenated polymer (holocellulose-92.82 wt%) present in the SGW. Similar observations have been reported in the literature [40-42].

Summary of the characteristics of bio-oil obtained is presented in Table 4. Water content determined using Karl Fischer volumetric titrator revealed that about 7.11-12.14 wt% moisture was present in the organic phase despite careful separation of the aqueous phase. The corresponding higher heating value (HHV-dry basis) of the organic phase computed using equation (4) below was found to be 28.45, 21.85, 19.75, 21.99, 25.31 and 20.64 MJ/kg for the case study (1, 2, 3, 4, 5 and 6).   Higher energy content recorded in the oil from the case study 1 and 5 is attributed to lower hydrogen/carbon ratio in the respective organic phase.

3.3   Chemical composition of bio-oil from GC-MS analysis

Identification of chemical compounds in the bio-oil samples was carried out by GC-MS. This result reveals that each bio-oil phase contain similar chemical compounds at various degrees. The compounds were identified using library search, MS NIST library 2011 and are summarized in Table 5 and 6. In order to evaluate the synergistic effect of the co-pyrolysis on the bio-oil chemical composition, the compounds were further classified as hydrocarbons; acids, aldehydes and ketones (AAK); benzene derivatives (phenolics, methoxy and hydroxy benzenes); and value added chemical (alcohols, esters and alkylsiloxanes, nitrogen and sulfur containing compounds) for the organic phase oil while the aqueous phase compounds were grouped in to AAK and value added chemicals (benzene derivatives, sugars, light hydrocarbons, esters and nitrogen containing compounds) as illustrated in Figure 5. The organic phase constituted predominantly benzene derivatives, which increased in the oil from co-pyrolysis relative to the oil from individual pyrolysis. Also, the composition of AAK in the organic phase decreased in the oil from co-pyrolysis compared to the oil from pyrolysis of the pure samples. The reduction of AKK in the oil can be attributed to the activity of minerals in the ash, which may have aided more decarboxylation, decarbonylation and dehydrogenation reactions of the bio-oil components. The

chemical compositions of the aqueous phase (Figure 5b) bio-oil was made up of mainly AAK and the value added chemicals. The AAK also decreased in the oil resulting from the co-pyrolysis process. This observation is also in good agreement with the result of ultimate analysis (Table 4) where reductions in the oxygen contents were observed. Co-pyrolysis oil obtained showed a superior quality compared to oil from the individual biomass which can serve as a good precursor for production of fuel, valuable chemicals and consumer products as presented in a schematic diagram in Figure 6.

4. Conclusions

This study provides background of co-pyrolysis of rice husk with underutilized biomass species in a fixed bed reactor. It gives experimental results on how synergism between different biomass feedstock during pyrolysis affect both yield, chemical and physicochemical properties of bio-oil. Two-phase bio-oil, organic and aqueous was collected in all the scenario investigated in this study. Higher bio-oil yield was recorded during the co-pyrolysis. The oil (both organic and the aqueous phases) from co-pyrolysis showed a superior quality and can be transformed to fuel, valuable chemicals and other consumer products. This study has demonstrated a good approach towards increasing valorisation of rice husk in a single reaction step.

References

1. Report of the Paris Conference on Climate Change (COP21) (2015) at: http://ec.europa.eu/clima/policies/international/negotiations/paris/index_en.htm. Accessed: 15th May, 2016

2. Aditiya, H.B., Chong, W.T., Mahlia, T.M.I., Sebayang, A.H., Berawi, M.A., Nur, H.: Second generation bioethanol potential from selected Malaysia's biodiversity biomasses: A review. Waste Management 47, Part A 46-61(2016)

3. Rachman, A., Rianse, U., Musaruddin, M., Pasolon, Y.: The Potential of Delivering Clean Locally Available Limitless Rice Husk Energy in the Celebes Island Indonesia. Energy Procedia 79, 55-60 (2015)

4. Pode, R., Diouf, B., Pode, G.: Sustainable rural electrification using rice husk biomass energy: A case study of Cambodia. Renewable and Sustainable Energy Reviews 44, 530-542 (2015)

5. Alias, A.B., Shallcross, D.C., Sharifah, A.S.A.K.: Rice husk combustion evolved gas analysis experiments and modelling. Biomass and Bioenergy 78, 36-47(2015)

6. Naghizadeh, F., Abdul Kadir, M. R., Doostmohammadi, A., Roozbahani, F., Iqbal, N., Taheri, M.M., Naveen, S.V., Kamarul, T.: Rice husk derived bioactive glass-ceramic as a functional bioceramic: Synthesis, characterization and biological testing. Journal of Non-Crystalline Solids 427, 54-61(2015)

7. Mohammed, I.Y., Abakr, Y.A., Kazi, F.K., Yusup, S., Alshareef, I., Chin, S.A.: Pyrolysis of Napier Grass in a Fixed Bed Reactor: Effect of Operating Conditions on Product Yields and Characteristics. BioResources 10(4), 6457-6478 (2015)

8. Bridgwater, A.V.: Review of Fast Pyrolysis of biomass and product upgrading, Biomass and Bioenergy 38, 68-94 (2012)

9. Eom, I.Y., Kim, J.Y., Lee, S.M., Cho, T.S., Yeo, H., Choi, J.W.: Comparison of pyrolytic products produced from inorganic-rich and demineralized rice straw (Oryzasativa L.) by fluidized bed pyrolyzer for future biorefinery approach. Bioresour. Technol.128, 664–672(2012)

10. Sharma, A., Rao, R.: Kinetics of pyrolysis of rice husk. Bioresour Technol 67(1) 53-59 (1999)

11. Ji-Lu, Z.: Bio-oil from fast pyrolysis of rice husk: yields and related properties and improvement of the pyrolysis system. Journal of Anal Appl Pyrolysis 80(1), 30-35(2007)

12. Naqvi, S. R., Uemura, Y., Osman, N.B., Yusup, S., Nuruddin, M.F. Physiochemical Properties of Pyrolysis Oil Derived from Fast Pyrolysis of Wet and Dried Rice Husk in a Free Fall Reactor. Applied Mechanics and Materials 625, 604-607 (2014) .

13. Zhai, M., Wang, X., Zhang, Y., Dong, P., Qi, G.: Characteristics of rice husk tar pyrolysis by external flue gas. International Journal of Hydrogen Energy 40(34), 10780-10787 (2015)

14. Zhai, M., Wang, X., Zhang, Y., Dong, P., Qi, G., Huang, Y.: Characteristics of rice husk tar secondary thermal cracking. Energy 93 Part 2, 1321-1327(2015)

15. Alvarez, J., Lopez, G., Amutio, M., Bilbao, J., Olazar, M.: Bio-oil production from rice husk fast pyrolysis in a conical spouted bed reactor. Fuel 128, 162-169 (2014)

16. Qian, Y., Zhang, J., Wang, J.: Pressurized pyrolysis of rice husk in an inert gas sweeping fixed-bed reactor with a focus on bio-oil deoxygenation. Bioresource Technology 174, 95-102 (2014)

17. Zhang, S., Dong, Q., Zhang, L., Xiong, Y.: Effects of water washing and torrefaction on the pyrolysis behavior and kinetics of rice husk through TGA and Py-GC/MS. Bioresource Technology 199, 352-361(2016)

18. Hsu, C-P., Huang, A-N., Kuo, H-P.: Analysis of the Rice Husk Pyrolysis Products from a Fluidized Bed Reactor. Procedia Engineering 102, 1183-1186 (2015)

19. Naqvi, S. R., Uemura, Y., Yusup, S.: Fast Pyrolysis of Rice Husk in a Drop Type Pyrolyzer for Bio-oil and Bio-char production, Aust. J. Basic & Appl. Sci. 8(5), 294-298 (2014)

20. Naqvi, S. R., Uemura, Y., Yusup, S., Sugiur, Y., Nishiyama, N., Naqvi, M.: The Role of Zeolite Structure and Acidity in Catalytic Deoxygenation of Biomass Pyrolysis Vapors, Energy Procedia 75, 793-800 (2015)

21. Naqvi, S. R., Uemura, Y., Yusup, S.: Catalytic pyrolysis of paddy husk in a drop type pyrolyzer for bio-oil production: The role of temperature and catalyst. Journal of Analytical and Applied Pyrolysis 106, 57-62 (2014)

22. Abu Bakar, M. S., Titiloye, J. O.: Catalytic pyrolysis of rice husk for bio-oil production. Journal of Analytical and Applied Pyrolysis 103, 362-368 (2013)

23. Mohammed, I.Y., Kazi, F.K., Yusup, S., Alaba, P.A., Sani, Y.M.. Abakr, Y.A.: Catalytic Intermediate Pyrolysis of Napier Grass in a Fixed Bed Reactor with ZSM-5, HZSM-5 and Zinc-Exchanged Zeolite-A as the Catalyst. Energies 9, 246 (2016).

24. Abnisa, F., Daud, W. M. A. W.: A review on co-pyrolysis of biomass: An optional technique to obtain a high-grade pyrolysis oil. Energy Conversion and Management 87, 71-85 (2014)

25. Martínez, J. D., Veses, A., Mastral, A. M., Murillo, R., Navarro, M.V., Puy, N., Artigues, A., Bartrolí, J., García, T.: Co-pyrolysis of biomass with waste tyres: Upgrading of liquid bio-fuel. Fuel Processing Technology 119, 263-271 , (2014)

26. Alvarez, J., Amutio, M., Lopez, G., Bilbao, J., Olazar, M.: Fast co-pyrolysis of sewage sludge and lignocellulosic biomass in a conical spouted bed reactor. Fuel 159, 810-818(2015)

27. Wu, Z., Wang, S., Zhao, J., Chen, L., Meng, H.: Thermochemical behavior and char morphology analysis of blended bituminous coal and lignocellulosic biomass model compound co-pyrolysis: Effects of cellulose and carboxymethylcellulose sodium. Fuel 171, 65-73 (2016)

28. Chen, W., Shi, S., Zhang, J., Chen, M., Zhou, X.: Co-pyrolysis of waste newspaper with high-density polyethylene: Synergistic effect and oil characterization. Energy Conversion and Management 112, 41-48 (2016)

29. Zaafouri, K., Trabelsi, A.B.H., Krichah, S., Ouerghi, A., Aydi, A., Claumann, C. A., Wüst, Z. A., Naoui, S., Bergaoui, L., Hamdi, M.: Enhancement of biofuels production by means of co-pyrolysis of Posidonia oceanica (L.) and frying oil wastes: Experimental study and process modeling. Bioresource Technology 207, 387-398 (2016)

30. Mohammed, I.Y., Abakr, Y.A., Kazi, F.K., Yusup, S., Alshareef, I., Chin, S.A.: Comprehensive Characterization of Napier Grass as a Feedstock for Thermochemical Conversion. *Energies* 8(5) 3403-3417 (2015)

31. Standard test method for water using volumetric Karl Fischer titration, ASTM E203, ASTM International, West Conshohocken, PA, USA (2001).

32 Mohammed, I.Y., Kazi, F. K., Abakr, Y.A., Yusuf, S., Razzaque, M.A.: Novel Method for the Determination of Water Content and Higher Heating Value of Pyrolysis Oil. BioResources 10(2), 2681-2690 (2015)

33. Chun Hsion, L., Mohammed, I. Y., Abakr, Y. A., Kazi, F. K., Yusup, S., Lam, H.L.:Element characteristic tolerance for semi-batch fixed bed biomass pyrolysis. Chemical Enginering Transactions 45, 1285-1290 (2015).

34. Mohammed, I.Y., Abakr, Y.A., Kabir, F., Yusup, S.: Effect of aqueous pretreatment on pyrolysis characteristics of Napier grass, Journal of Engineering Science & Technology 10(11) 1487 – 1496 (2015)

35. Yakub, M.I., Abdalla, A.Y., Feroz, K.K., Suzana, Y., Ibraheem, A., Chin, S.A.: Pyrolysis of Oil Palm Residues in a Fixed Bed Tubular Reactor, Journal of Power and Energy Engineering 3(04) 185 (2015)

36. Bordoloi, N., Narzari, R., Chutia, R.S., Bhaskar, T., Kataki, R.: Pyrolysis of Mesua ferrea and Pongamia glabra seed cover: Characterization of bio-oil and its sub-fractions. Bioresource Technology 178, 83–89 (2015)

37. Deshmukh, Y., Yadav, V., Nigam, N., Yadav, A., Khare, P.: Quality of bio-oil by pyrolysis of distilled spent of Cymbopogon flexuosus. Journal of Analytical and Applied Pyrolysis 2015; *in press*

38. Wang, Z., Wang, F., Cao, J., Wang, J.: Pyrolysis of pine wood in a slowly heating fixed-bed reactor: potassium carbonate versus calcium hydroxide as a catalyst.Fuel Process. Technol. 91 (8), 942–950 (2010)

39. Lin, Y.Y., Zhang, C., Zhang, M.C., Zhang, J.A.: Deoxygenation of bio-oil during pyrolysis of biomass in the presence of CaO in a fluidized-bed reactor. Energy Fuels 24, 5686–5695 (2010)

40. Couher, C. Commandre, J.M., Salvador, S.: Failure of the component additivity rule to predict gas yields of biomass in flash pyrolysis at 950 °C. Biomass Bioenergy 33, 316–326 (2009)

41. Couher, C., Commandre, J.M., Salvador, S.: Is it possible to predict gas yields of any biomass after rapid pyrolysis at high temperature from its composition in cellulose, hemicelluloses and lignin? Fuel 88, 408–417 (2009)

42. Mohammad, I. J., Mohammad, G.R., Ashfaque A.C., Nanjappa, A.: Biofuels Production through Biomass Pyrolysis —A Technological Review. Energies 5, 4952-5001 (2012)

Table 1: Composition of feedstock used

Biomass	Case study					
	1	2	3	4	5	6
NG (wt%)	100	0	0	50	0	30
RH (wt%)	0	100	0	50	50	40
SGW(wt%)	0	0	100	0	50	30

Table 2: Characteristics of feedstock

Case study	AC	VM	FC	C	H	N	S	O	HHV
				wt% dry basis					MJ/kg
1	1.75±0.04	81.51±0.26	16.74±0.05	51.61±0.24	6.01±0.02	0.99±0.01	0.32±0.01	41.07±0.02	18.05±0.07
2	13.16±0.58	72.27±0.22	14.57±0.04	40.67±0.23	6.79±0.02	0.44±0.01	0.87±0.01	51.23±0.04	16.56±0.05
3	10.82±0.46	79.97±0.26	9.21±0.03	44.62±0.23	6.67±0.02	0.19±0.01	0.00	48.52±0.03	17.02±0.06
4	7.45±0.33	76.89±0.24	15.66±0.04	46.14±0.23	6.40±0.02	0.71±0.01	0.60±0.01	46.15±0.02	17.30±0.06
5	12.39±0.62	75.72±0.24	11.89±0.02	42.16±0.23	6.70±0.02	0.32±0.01	0.43±0.01	50.39±0.04	17.81±0.06
6	9.27±0.42	75.33±0.25	15.40±0.04	43.65±0.23	6.50±0.02	0.53±0.01	0.44±0.01	48.88±0.03	17.76±0.06

(AC): Ash content; (VM): volatile matter; (FC): fixed carbon; (C): carbon; (H): hydrogen; (N): nitrogen; (S): sulfur; (O): oxygen; (HHV): higher heating value. Values are the means (n=3) ± standard deviation

Table 3: Mineral composition of the ash

Minerals (mg/kg)	Case study					
	1	2	3	4	5	6
K	3079.51±224.80	174.08±3.23	474.98±9.11	1077.85±81.10	316.181±29.44	673.241±38.34
Ca	206.71±13.20	31.91±2.36	1247.40±69.63	80.01±4.22	211.86±22.90	144.79±12.67
Si	206.0±25.13	2641.57±116.59	860.55±21.03	1835.45±66.21	2335.±101.23	2030.35±95.71

Values are the means (n=3) ± standard deviation(mg/kg)

Table 4: Properties of bio-oil product

Organic phase

Case study	C	H	N	S	O	H₂O	LHV
	wt%						MJ/kg
1	50.74 ± 0.81	6.22 ± 0.13	0.78 ± 0.03	0.60 ± 0.01	41.66 ± 0.78	7.24 ± 0.12	26.23 ± 0.10
2	39.99 ± 0.67	8.43 ± 0.15	0.43 ± 0.03	0.16 ± 0.01	50.99 ± 0.91	8.81 ± 0.15	19.73 ± 0.10
3	42.95 ± 0.68	8.30 ± 0.15	1.66 ± 0.05	0.03 ± 0.01	47.06 ± 0.90	8.20 ± 0.15	17.95 ± 0.10
4	48.39 ± 0.71	7.30 ± 0.14	1.66 ± 0.05	1.12 ± 0.04	41.53 ± 0.78	7.78 ± 0.12	20.11 ± 0.10
5	46.05 ± 0.68	5.50 ± 0.13	0.14 ± 0.01	1.58 ± 0.06	46.73 ± 0.88	7.11 ± 0.12	23.35 ± 0.10
6	46.23 ± 0.69	6.82 ± 0.14	2.30 ± 0.07	1.88 ± 0.06	42.77 ± 0.78	12.14 ± 0.19	17.87 ± 0.10

Aqueous phase

Case study	C	H	N	S	O	H₂O	LHV
	wt%						MJ/kg
1	15.27 ± 0.22	12.20 ± 0.20	1.45 ± 0.04	1.70 ± 0.04	69.38 ± 1.28	69.38 ± 1.20	14.44 ± 0.10
2	14.41 ± 0.22	12.52 ± 0.20	1.50 ± 0.04	1.76 ± 0.04	69.81 ± 1.28	73.42 ± 1.24	12.11 ± 0.10
3	17.22 ± 0.25	13.66 ± 0.20	0.54 ± 0.01	0.44 ± 0.01	68.14 ± 1.28	71.51 ± 1.24	13.34 ± 0.10
4	17.24 ± 0.25	14.57 ± 0.20	1.06 ± 0.02	1.90 ± 0.04	65.23 ± 1.28	62.42 ± 1.20	13.88 ± 0.10
5	17.89 ± 0.25	14.81 ± 0.20	0.75 ± 0.01	1.88 ± 0.04	64.67 ± 1.28	61.08 ± 1.20	14.58 ± 0.10
6	17.27 ± 0.25	15.89 ± 0.20	1.50 ± 0.04	1.70 ± 0.04	63.64 ± 1.28	62.41 ± 1.20	13.87 ± 0.10

(C): carbon; (H): hydrogen; (N): nitrogen; (S): sulfur; (O): oxygen; (LHV): lower heating value. Values are the means (n=3) ± standard deviation

Table 5: List of identified chemical compounds in the bio-oil organic phase

RT (min)	Compound name	Formula	Case study-peak area(%)					
			1	2	3	4	5	6
3.02	3-CYCLOHEXENE-1-PROPANAL	$C_9H_{14}O$	-	-	2.81	-	-	-
3.02	3-CYCLOHEXENE-1-METHANOL, 6-HYDROXY-, CIS-	$C_7H_{12}O_2$	-	-	-	1.96	-	-
3.24	CYCLOBUTENE, 2-PROPENYLIDENE-	C_7H_8	-	-	3.19	2.01	-	-
3.82	BICYCLO[2.2.1]HEPTANE, 2-ETHYL-	C_9H_{16}	-	-	-	-	-	-
3.82	3-FURANCARBOXYLIC ACID, METHYL ESTER	$C_6H_6O_3$	-	4.29	-	3.41	-	-
3.82	FURAN, 2,5-DIMETHYL-	C_6H_8O	-	-	-	-	3.85	-
3.83	DICYCLOHEXYLMETHANOL	$C_{13}H_{24}O$	-	-	-	3.41	-	-
3.83	1,1-DIVINYL-1-SILACYCLOBUTANE	$C_7H_{12}Si$	-	-	7.36	-	-	-
3.85	L-HISTIDINE, 3-METHYL-	$C_7H_{11}O_2N_3$	4.66	-	-	-	-	-
3.99	2-FURANMETHANOL	$C_5H_6O_2$	-	-	-	-	-	-
4.03	3-FURANMETHANOL	$C_5H_6O_2$	3.04	2.64	-	1.68	2.89	-
4.98	2-FURANCARBOXALDEHYDE, 5-METHYL-	$C_6H_6O_2$	-	-	2.51	-	-	-
5.10	N-VINYLIMIDAZOLE	$C_5H_6N_2$	-	8.50	-	-	-	-
5.11	PHENOL	C_6H_6O	-	-	10.66	7.75	6.47	7.95
5.13	CARBONIC ACID, 2-METHOXYETHYL PHENYL ESTER	$C_{10}H_{12}O_4$	8.40	-	-	-	-	-
5.52	2-ETHYL-5-PROPYLCYCLOPENTANONE	$C_{10}H_{18}O$	-	-	-	2.14	2.51	-
5.52	1,2-CYCLOPENTANEDIONE, 3-METHYL-	$C_6H_8O_2$	-	1.94	2.29	-	-	-
5.54	CYCLOHEXANONE, 5-METHYL-2-(1-METHYLETHYL)-, TRANS-	$C10H_{18}O$	1.95	-	-	-	-	-
5.74	PHENOL, 2-METHYL-	C_7H_8O	4.05	5.14	6.77	5.14	4.48	7.27
5.90	P-CRESOL	C_7H_8O	-	8.25	7.87	7.44	6.90	-
5.93	PHENOL, 3-METHYL-	C_7H_8O	4.94	-	-	-	-	9.14
6.04	ETHANONE, 1-(1-CYCLOHEXEN-1-YL)-	$C_8H_{12}O$	7.62	8.58	-	-	-	-
6.04	PHENOL, 2-METHOXY-	C_7H_8O2	-	-	6.24	7.80	7.73	7.27
6.25	BENZALDEHYDE, 2-(2-PROPYNYLOXY)-	$C_{10}H_8O_2$	-	-	2.03	-	-	-
6.26	CYCLOPENTANOL, 1,2-DIMETHYL-3-(1-METHYLETHENYL)-, [1R-(1.ALPHA.,2.BETA	$C_{10}H_{18}O$	-	-	-	1.79	-	-
6.27	1H-1,3-BENZIMIDAZOL-7-AMINE, N-[(4-METHOXYPHENYL)METHYL]-2-METHYL-	$C_{16}H_{17}ON_3$	1.82	-	-	-	-	-
6.49	PHENOL, 2,5-DIMETHYL-	$C_8H_{10}O$	2.49	3.46	4.25	3.51	3.23	6.13

RT	Compound	Formula						
6.61	PHENOL, 3-ETHYL-	$C_8H_{10}O$	8.17	10.15	10.09	9.95	8.37	8.20
6.83	PHENOL, 2-METHOXY-3-METHYL-	$C_8H_{10}O_2$	3.67	6.15	3.48	5.52	8.98	5.31
7.01	1,2-BENZENEDIMETHANOL	$C_8H_{10}O_2$	-	8.99	-	-	-	-
7.01	BENZOFURAN, 2,3-DIHYDRO-	C_8H_8O	-	-	5.77	7.45	-	3.20
7.03	BENZALDEHYDE, 2-METHYL-	C_8H_8O	13.37	-	-	-	10.08	-
7.15	PHENOL, 3-ETHYL-5-METHYL-	$C_9H_{12}O$	-	1.71	-	2.19	-	-
7.45	PHENOL, 4-ETHYL-2-METHOXY-	$C_9H_{12}O_2$	5.37	5.68	4.68	5.85	6.34	5.37
7.71	2-METHOXY-4-VINYLPHENOL	$C_9H_{10}O_2$	6.72	7.97	-	5.71	7.88	4.01
7.71	PHENOL, 2,3,5,6-TETRAMETHYL-	$C_{10}H_{14}O$	-	-	4.12	-	-	-
7.94	PHENOL, 2,6-DIMETHOXY-	$C_8H_{10}O_3$	8.83	4.08	6.10	6.10	4.96	3.74
8.57	1,2,4-TRIMETHOXYBENZENE	$C_9H_{12}O_3$	2.17	-	2.26	-	-	-
8.61	PHENOL, 2-METHOXY-4-(1-PROPENYL)-	$C_{10}H_{12}O_2$	2.44	3.94	-	3.07	4.08	3.49
8.84	1,4-DIMETHOXY-2,3-DIMETHYLBENZENE	$C_{10}H_{14}O_2$	-	-	-	-	-	-
8.84	5,6-DIPROPYL-4-HEXYL-2H-PYRAN-2-ONE	$C_{17}H_{28}O_2$	-	-	-	-	2.03	-
8.87	3-LAURAMIDOBENZOIC ACID	$C_{19}H_{29}O_3N$	-	-	-	-	-	-
9.01	4-ETHYLBIPHENYL	$C_{14}H_{14}$	-	-	-	-	-	3.24
9.05	5-TERT-BUTYLPYROGALLOL	$C_{10}H_{14}O3$	2.52	-	2.06	1.86	-	-
9.08	BENZENEAMINE, 3-ETHYL-4-HYDROXY-	C8H11ON	-	2.60	-	1.47	2.08	-
10.06	PHENOL, 2,6-DIMETHOXY-4-(2-PROPENYL)-	$C_{11}H_{14}O_3$	3.11	1.67	-	0.83	2.95	-
10.22	1,2,3,4,7-PENTAMETHYLINDOLE	C13H17N	-	-	-	-	-	3.11
11.67	SILICIC ACID, DIETHYL BIS(TRIMETHYLSILYL) ESTER	$C_{10}H_{28}O_4Si_3$	-	-	-	-	-	3.04
11.85	SILICIC ACID, DIETHYL BIS(TRIMETHYLSILYL) ESTER	$C_{10}H_{28}O_4Si_3$	-	-	-	-	-	3.32
12.02	SILICIC ACID, DIETHYL BIS(TRIMETHYLSILYL) ESTER	$C_{10}H_{28}O_4Si_3$	-	-	-	-	-	3.59
12.04	CYCLOTRISILOXANE, HEXAMETHYL-	$C_6H_{18}O_3Si_3$	-	2.26	-	-	-	-
12.05	OCTASILOXANE, 1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-HEXADECAMETHYL-	$C_{16}H_{50}O_7Si_8$	-	-	-	0.18	-	4.88
12.16	HEPTASILOXANE, 1,1,3,3,5,5,7,7,9,9,11,11,13,13-TETRADECAMETHYL-	$C_{14}H_{44}O_6Si_7$	-	-	-	-	2.00	-
12.37	CYCLOTRISILOXANE, HEXAMETHYL-	$C_6H_{18}O_3Si_3$	-	2.00	-	-	-	-
12.52	OCTASILOXANE, 1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-HEXADECAMETHYL-	$C_{16}H_{50}O_7Si_8$	-	-	-	-	-	4.17
18.97	1,4-BENZENEDICARBOXYLIC ACID, BIS(2-ETHYLHEXYL) ESTER	$C_{24}H_{38}O_4$	-	-	-	-	-	-

RT	Compound name	Formula	1	2	3	4	5	6
19.06	1,3-BENZENEDICARBOXYLIC ACID, BIS(2-ETHYLHEXYL) ESTER	$C_{24}H_{38}O_4$	4.67	-	5.47	-	-	3.56
20.56	HEXANEDIOIC ACID, BIS[2-(2-BUTOXYETHOXY)ETHYL] ESTER	$C_{22}H_{42}O_8$	-	-	-	-	-	-
20.57	DI(BUTOXYETHYL)ADIPATE	$C_{18}H_{34}O_6$	-	-	-	1.76	2.19	-

Table 6: List of identified chemical compounds in the bio-oil aqueous phase

RT (min)	Compound name	Formula	Case study-peak area(%)					
			1	2	3	4	5	6
3.24	1,4,7-TRIOXA-10-AZACYCLODODECANE	$C_8H_{17}O_3N$	-	-	-	-	3.50	-
3.29	PROPANOIC ACID, 1-METHYLPROPYL ESTER	$C_7H_{14}O_2$	-	-	3.24	-	-	2.88
3.31	1,2,4,5-CYCLOHEXANETETROL, (1.ALPHA.,2.ALPHA.,4.ALPHA.,5.BETA.)-	$C_6H_{12}O_4$	3.24	-	-	-	-	-
3.45	FORMIC ACID, 3-METHYLPENTYL ESTER	$C_7H_{14}O_2$	-	-	3.48	-	-	3.49
3.81	1H-FLUORENE, DODECAHYDRO-	$C_{13}H_{22}$	-	-	-	4.78	-	-
3.82	1,1-DIVINYL-1-SILACYCLOBUTANE	$C_7H_{12}Si$	-	3.91	-	-	-	-
3.82	3-(BUT-3-ENYL)-CYCLOHEXANONE	$C_{10}H_{16}O$	-	-	10.36	-	-	-
3.84	1H-INDENE, OCTAHYDRO-, CIS-	C_9H_{16}	-	-	-	-	-	5.60
3.85	CARBONIC ACID, 2,2,2-TRICHLOROETHYL CYCLOHEXYLMETHYL ESTER	$C_{10}H_{15}O_3Cl_3$	8.65	-	-	-	7.27	-
4.00	1H-IMIDAZOLE-2-METHANOL	$C_4H_6ON_2$	-	3.50	7.27	4.34	6.16	7.35
4.06	Z,Z-6,28-HEPTATRIACTONTADIEN-2-ONE	$C_{37}H_{70}O$	6.51	-	-	-	-	-
4.48	2,4-DIMETHYLFURAN	C_6H_8O	-	-	3.64	-	-	-
4.52	CYCLOHEXENE, 3,5-DIMETHYL-	C_8H_{14}	4.28	-	-	-	-	-
4.52	CARBONIC ACID, ETHYL UNDEC-10-ENYL ESTER	$C_{14}H_{26}O_3$	-	-	-	3.14	-	-
4.53	2-ACETYLPIPERIDINE	$C_7H_{13}ON$	-	-	-	-	4.23	-
4.53	N-METHYL-3-PIPERIDINECARBOXAMIDE	$C_7H_{14}ON_2$	-	2.38	-	-	-	-
4.55	2-PENTANONE, 5-(DIETHYLAMINO)-	$C_9H_{19}ON$	-	-	-	-	-	4.25

4.55	CYCLOPENTANONE, 2-(1-METHYLPROPYL)-	$C_9H_{16}O$	-	-	2.57	-	-	-
4.58	BUT-3-EN-1-YL 2-METHYLBUTANOATE	$C_9H_{16}O_2$	3.86	-	-	-	-	-
4.64	2-TERT-BUTYLCYCLOHEXANONE	$C_{10}H_{18}O$	-	-	-	2.28	-	-
4.66	3-(1'-PYRROLIDINYL)-2-BUTANONE	$C_8H_{15}ON$	-	-	4.60	-	3.02	-
4.70	UNDECANOIC ACID, 11-MERCAPTO-	$C_{11}H_{22}O_2S$	4.03	-	-	-	-	-
4.97	2-FURANCARBOXALDEHYDE, 5-METHYL-	$C_6H_6O_2$	-	-	4.03	-	-	-
5.02	2-CYCLOPENTEN-1-ONE, 3-METHYL-	C_6H_8O	-	-	2.59	-	-	-
5.11	BIS(2-CHLOROETHYL) ETHER	$C_4H_8OCl_2$	-	2.96	7.29	-	-	-
5.15	PHOSPHONIC ACID, (P-HYDROXYPHENYL)-	$C_6H_7O_4P$	6.25	-	-	4.59	5.16	5.95
5.26	2-PROPANAMINE, N-METHYL-1-[4-[3-(1-PIPERIDYL)PROPOXY]PHENYL]-	$C_{18}H_{30}ON_2$	-	-	-	-	-	4.64
5.29	2,3-DIHYDRO-2-METHYL-5-ETHYLFURAN	$C_7H_{12}O$	-	-	3.00	-	-	-
5.36	FURAN, TETRAHYDRO-2,5-DIMETHOXY-	$C_6H_{12}O_3$	2.75	-	-	-	-	-
5.52	2-ETHYL-5-PROPYLCYCLOPENTANONE	$C_{10}H_{18}O$	5.11	2.92	6.26	4.09	5.30	5.28
5.74	PHENOL, 2-METHYL-	C_7H_8O	-	2.09	5.47	2.67	3.22	3.30
5.90	4-IMIDAZOLACETIC ACID, BUTYL ESTER	$C_9H_{14}O_2N_2$	-	-	4.09	-	-	-
5.91	PHENOL, 2-METHYL-	C_7H_8O	-	3.73	-	3.50	4.33	8.12
6.03	(2,3-DICHLOROPHENYL)CARBAMIC ACID 4-METHOXYPHENYL ESTER	$C_{14}H_{11}O_3NCl_2$	-	-	6.20	-	-	-
6.04	PHENOL, 2-METHOXY-	$C_7H_8O_2$	-	3.29	-	4.75	5.73	6.50
6.06	IMIDAZOLE, 2-AMINOCARBONYL-1-METHYL-	$C_5H_7ON_3$	7.14	-	-	-	-	-
6.12	HEPTANE, 1,1'-OXYBIS-	$C_{14}H_{30}O$	-	-	-	3.26	5.24	-
6.15	CYCLOHEXANEMETHYL PROPANOATE	$C_{10}H_{18}O_2$	-	-	-	-	-	3.51
6.17	1-SILACYCLO-2,4-HEXADIENE	C_5H_8Si	-	-	-	-	-	3.55
6.28	1,2,4-CYCLOPENTANETRIONE, 3-METHYL-	$C_6H_6O_3$	-	-	-	-	-	3.42
6.49	4,5,6,6A-TETRAHYDRO-2(1H)-PENTALENONE	$C_8H_{10}O$	-	0.93	-	-	-	-
6.61	PHENOL, 2,3-DIMETHYL-	$C_8H_{10}O$	-	1.68	2.87	2.47	2.95	-
6.64	1,3,5-CYCLOHEPTATRIENE, 1-METHOXY-	$C_8H_{10}O$	4.22	-	-	-	-	-
6.83	2,3-DIMETHYLHYDROQUINONE	$C_8H_{10}O_2$	-	6.02	-	-	-	-
6.83	2-CYCLOPENTEN-1-ONE, 2,3,4,5-TETRAMETHYL-	$C_9H_{14}O$	-	-	-	10.14	-	-
6.83	2-METHOXY-5-METHYLPHENOL	$C_8H_{10}O_2$	-	-	-	-	14.09	-
6.84	PENTANOIC ACID, 2-ETHYLCYCLOHEXYL ESTER	$C_{13}H_{24}O_2$	-	-	10.28	-	-	-

| RT	Compound	Formula						
6.84	BENZENE, 1-ETHOXY-2-METHOXY-4-METHYL-	$C_{10}H_{14}O_2$	-	-	-	-	-	8.22
6.91	2-PROPENAMIDE, N-(4-AMINOBUTYL)-3-(3,4-DIHYDROXYPHENYL)-, (E)-	$C_{13}H_{18}O_3N_2$	11.20	-	-	-	-	-
7.01	1,4:3,6-DIANHYDRO-.ALPHA.-D-GLUCOPYRANOSE	$C_6H_8O_4$	-	2.53	3.77	4.11	3.04	4.42
7.04	BENZENE, (ETHENYLOXY)-	C_8H_8O	5.31	-	0.00	0.00	-	-
7.07	4-MERCAPTOPHENOL	C_6H_6OS	-	-	3.12	2.42	-	-
7.15	CYCLOPENTANECARBOXYLIC ACID, 2-ETHYLHEXYL ESTER	$C_{14}H_{26}O_2$	-	-	-	2.35	-	-
7.15	CYCLOPENTANECARBOXYLIC ACID, 4-ISOPROPYLPHENYL ESTER	$C_{15}H_{20}O_2$	-	0.94	-	0.00	-	-
7.16	BUTANOIC ACID, 3,7-DIMETHYL-2,6-OCTADIENYL ESTER, (E)-	$C_{14}H_{24}O_2$	-	-	-	-	-	3.20
7.38	1,2-BENZENEDIOL, 3-METHOXY-	$C_7H_8O_3$	5.91	-	-	2.66	4.36	-
7.39	HYDROQUINONE	$C_6H_6O_2$	-	-	-	-	3.35	-
7.45	4-HYDROXY-2,4,5-TRIMETHYL-2,5-CYCLOHEXADIEN-1-ONE	$C_9H_{12}O_2$	-	1.29	-	-	-	-
7.45	3,4-DIHYDROXYACETOPHENONE	$C_8H_8O_3$	-	-	-	-	-	5.67
7.71	4-(3,7,7-TRIMETHYL-2-OXABICYCLO[3.2.0]HEPT-3-EN-1-YL)BUT-3-EN-2-ONE	$C_{13}H_{18}O_2$	-	0.86	-	-	-	-
7.94	FORMIC ACID, 2,6-DIMETHOXYPHENYL ESTER	$C_9H_{10}O_4$	-	2.76	-	-	-	-
7.96	PHENOL, 2,6-DIMETHOXY-	$C_8H_{10}O_3$	9.14	-	5.86	3.45	5.14	5.43
8.56	PHENOL, 4-METHOXY-3-(METHOXYMETHYL)-	$C_9H_{12}O_3$	3.37	-	-	-	-	-
8.61	PHENOL, 2-METHOXY-4-(1-PROPENYL)-, (Z)-	$C_{10}H_{12}O_2$	-	0.57	-	-	-	-
8.95	D-ALLOSE	$C_6H_{12}O_6$	-	55.08	-	28.33	9.25	5.23
9.04	BENZENE, 1,2,3-TRIMETHOXY-5-METHYL-	$C_{10}H_{14}O_3$	2.14	-	-	-	-	-
9.08	2-PROPANONE, 1-(4-HYDROXY-3-METHOXYPHENYL)-	$C_{10}H_{12}O_3$	2.51	1.47	-	-	2.75	-
9.19	.ALPHA.-D-GLUCOPYRANOSE, 4-O-.BETA.-D-GALACTOPYRANOSYL-	$C_{12}H_{22}O_{11}$	-	1.10	-	4.61	1.91	-
9.48	LACTOSE	$C_{12}H_{22}O_{11}$	-	-	-	2.06	-	-
10.08	PHENOL, 2,6-DIMETHOXY-4-(2-PROPENYL)-	$C_{11}H_{14}O_3$	2.02	-	-	-	-	-
10.42	BENZENEMETHANOL, 2,5-DIMETHOXY-, ACETATE	$C_{11}H_{14}O_4$	2.34	-	-	-	-	-
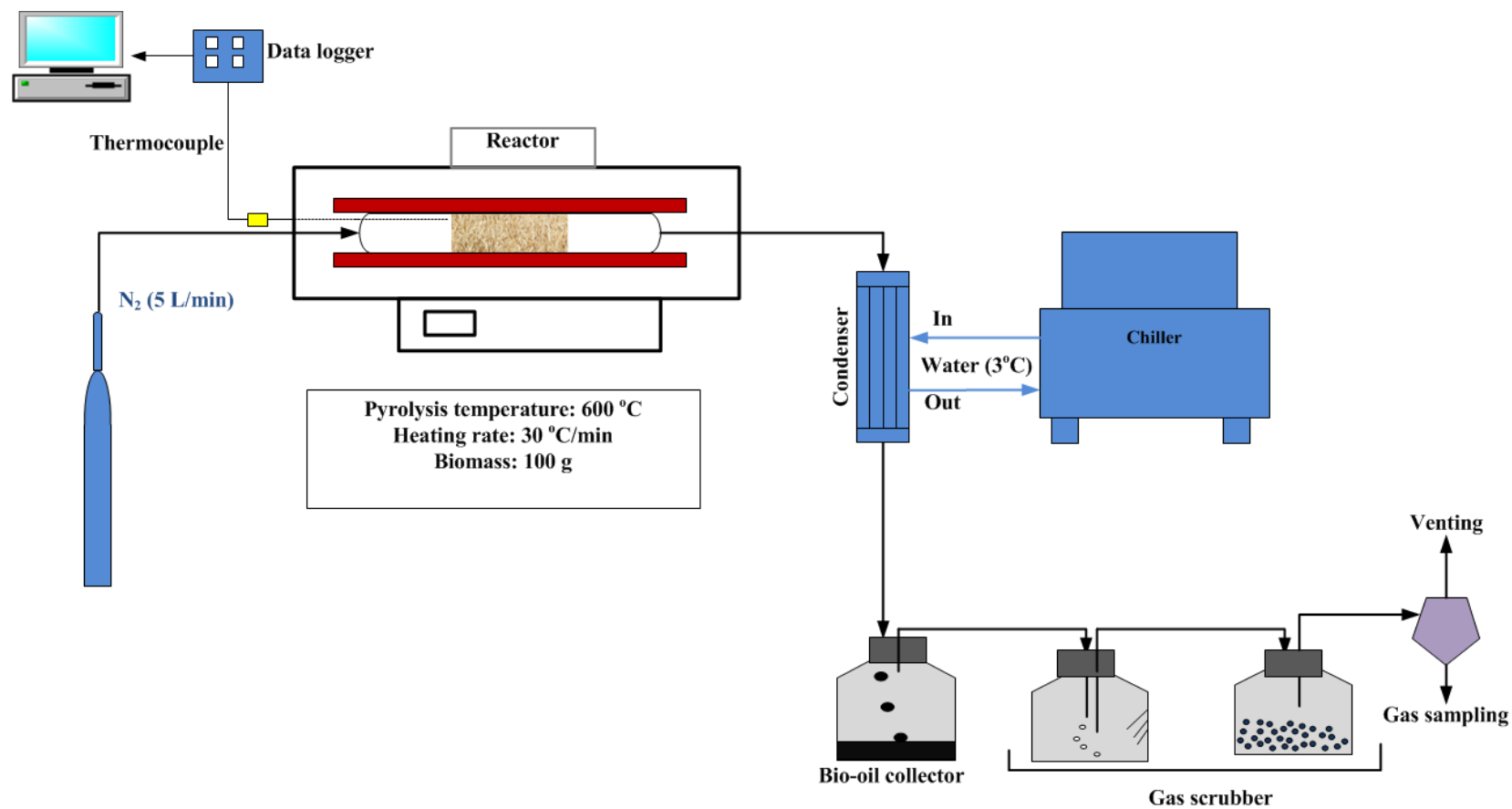
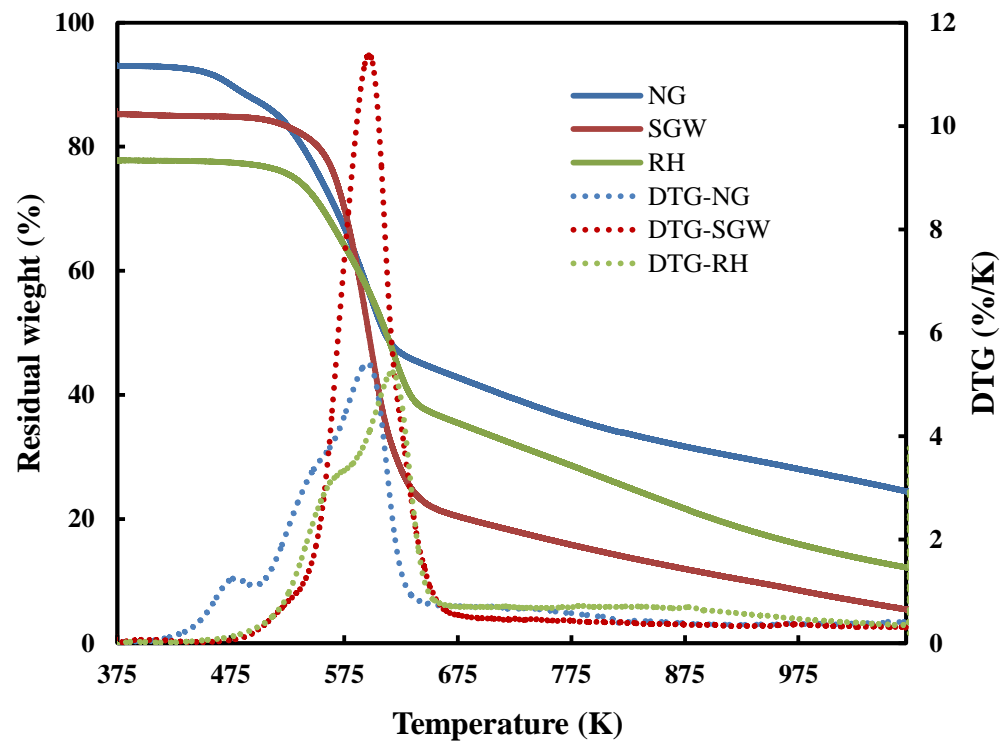**Figure 1**: Schematic diagram of Pyrolysis experimental setup.

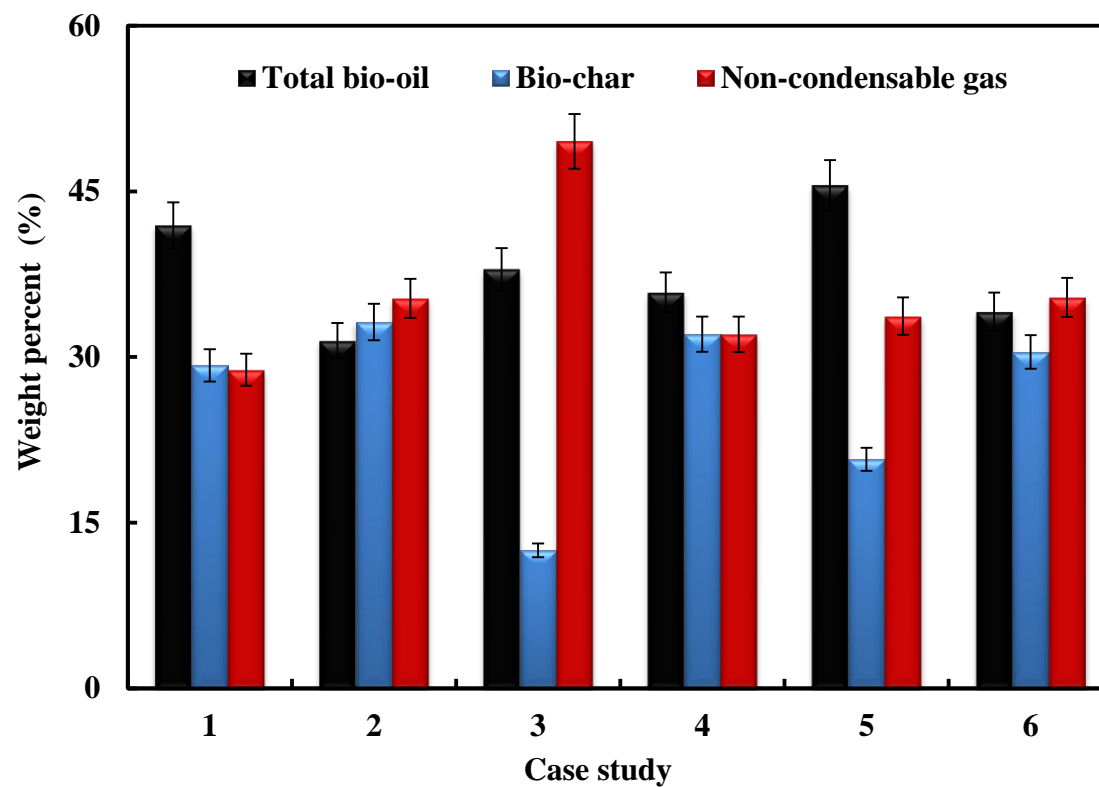**Figure 2**: TG and DTG of the NG, GW and RH. Condition: nitrogen atmosphere (20 mL/min), heating rate (10 K/min).

Figure 3: Pyrolysis product distribution (600 ^{o}C, 5 L/min N_2 flow and 30 ^{o}C/min heating rate). Values are the means± SD
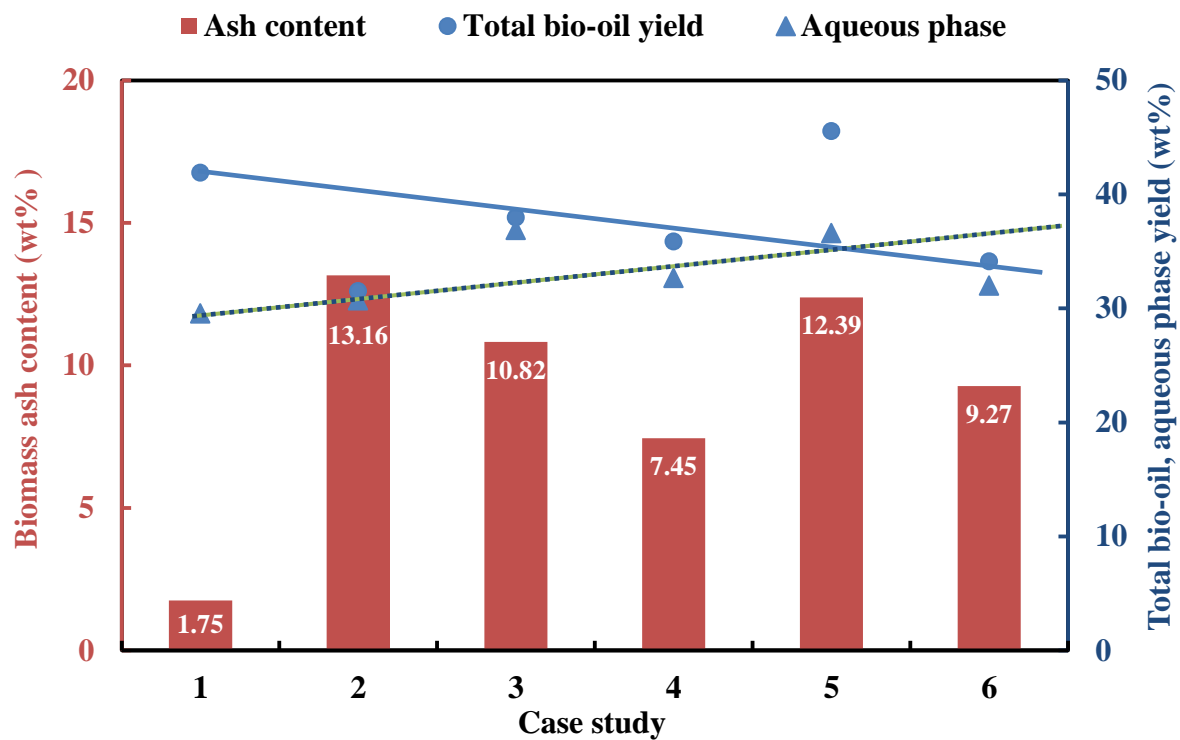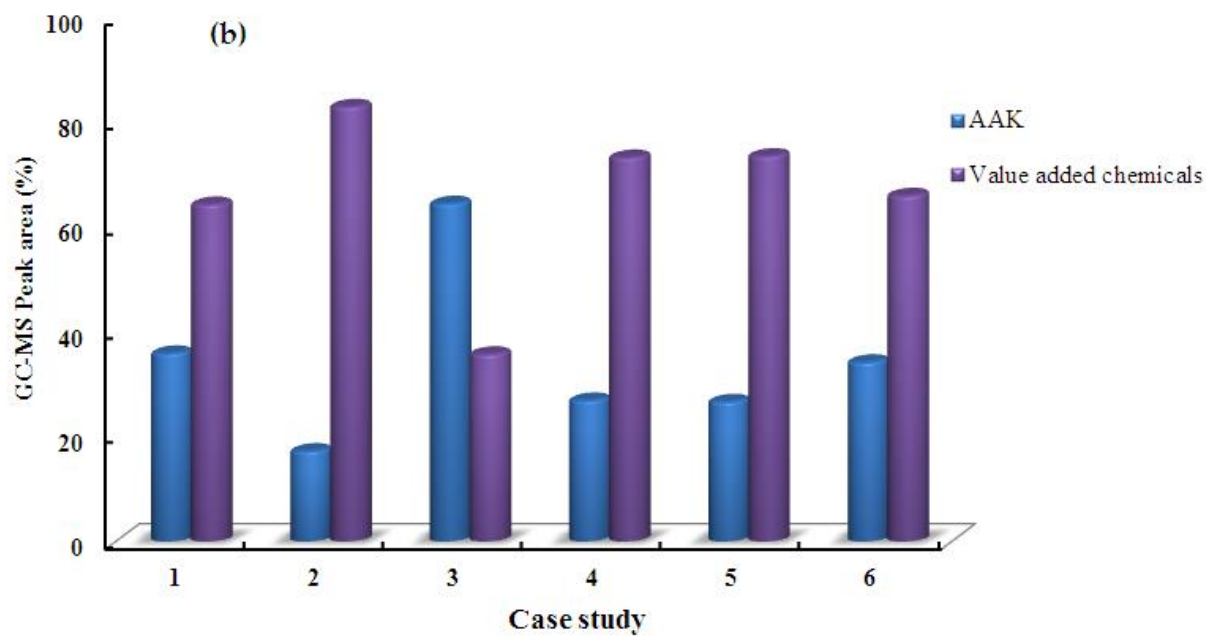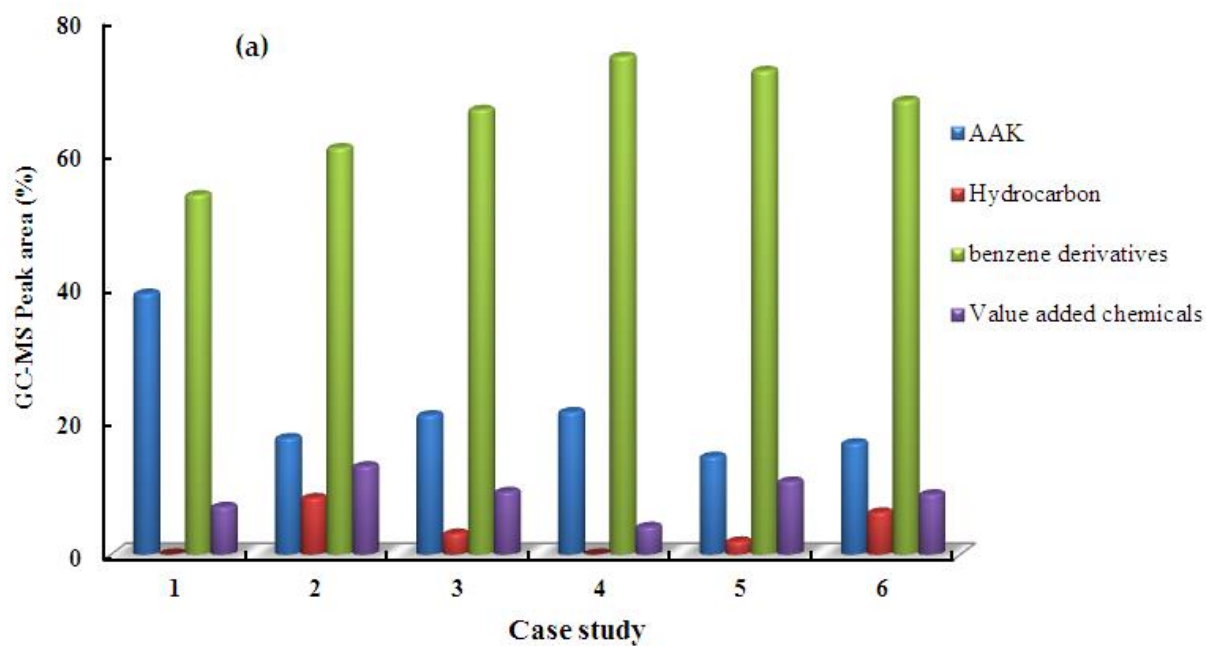
Figure 4: Relationship between biomass ash, total bio-oil yield and aqueous phase. Values are the means of three replicates
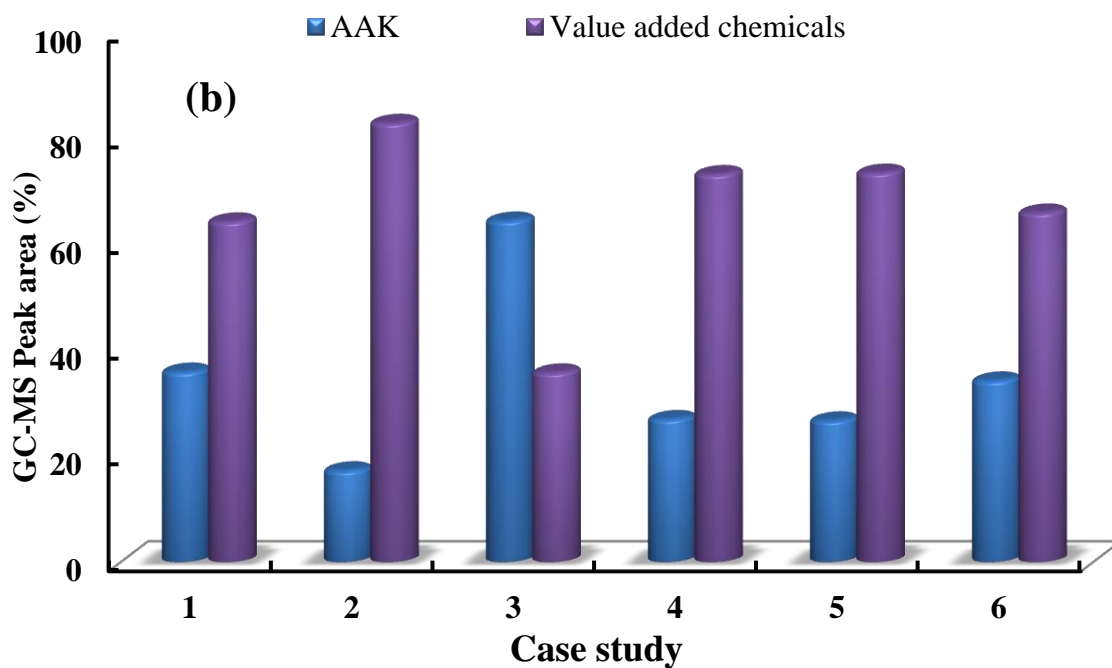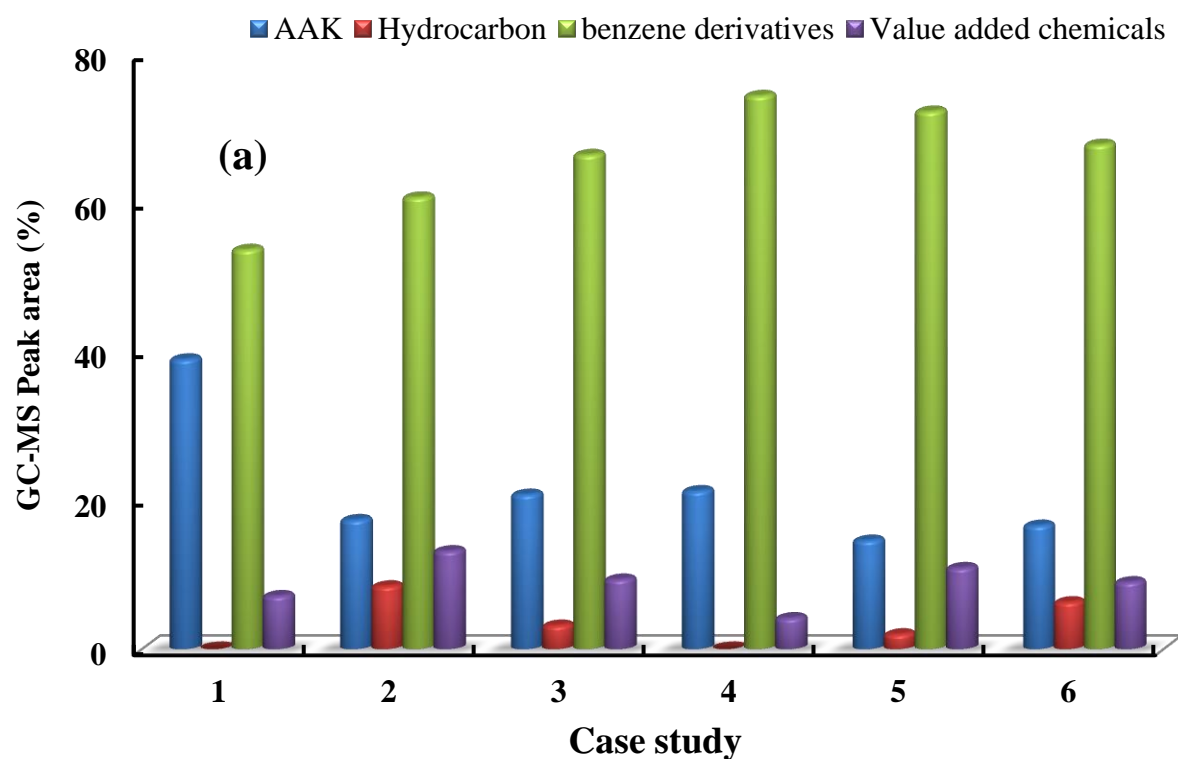
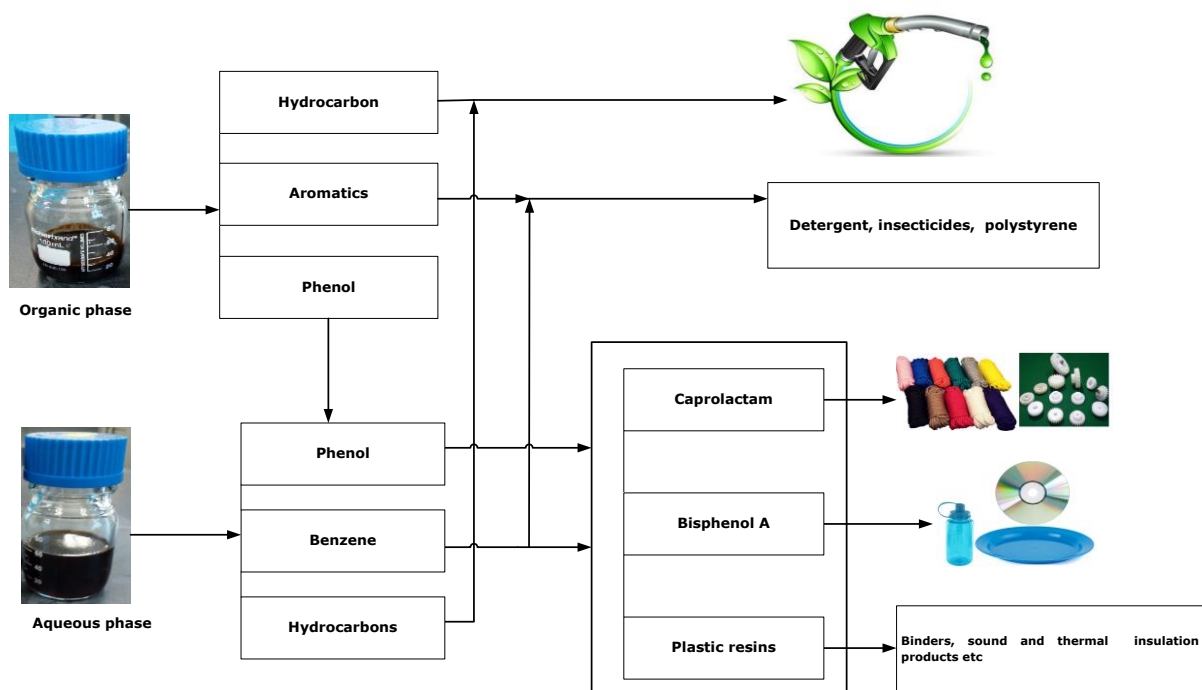**Figure 5**: Groups of chemical compounds identified in the bio-oil (a) organic and (b) aqueous

Figure 6: Schematic diagram showing possible product that can be derived from the bio-oil