

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

--Manuscript Draft--

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Abstract:	<p>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 600oC, 30oC/min and 5L/min nitrogen flowrate. Two phase bio-oil (organic and aqueous) was collected and characterized using standard analytical techniques. 34.13-45.55wt % total boil-oil yield was recorded using assorted biomass compared to pure risk husk biomass with 31.51wt% 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.</p>	
Response to Reviewers:	<p>Response to Reviewers</p> <p>We would like to thank the reviewers for their comments on this paper. Below we respond to each of the points raised, which we believe has improved the paper.</p> <p>Reviewer 1 Comment 1: The authors have done a good piece of work and they have demonstrated the valorisation of rice husk for the production of high grade bio-oil, which can be transformed into fuel and valuable chemicals. While I find this work worthwhile, it could be improved upon if the following comments are taken into</p>	

consideration:

- Need to check English language and spellings thoroughly
- In the results and discussion section the authors should bring out the significance of low ash content in the characterisation of their samples.
- Please ensure that you indicate for each applicable graph/figure and table the number of times that the experiment was repeated to obtain the reported values.
- Also incorporate standard deviation/% error where required. Ensure that this information (number of times repeated) is also included in the respective experimental sections.

Response 1: Many thanks for the suggestions. All the issues raised have been addressed and the manuscript updated accordingly.

Reviewer 2: The article is well written. The authors must check the format, especially spacing between units and numbers.

Response 2: Thank you. All this points raised have been addressed in the manuscript.

Reviewer 3: The manuscript presents some interesting information on co-pyrolysis of Rice Husk with Napier grass and sago waste. Some minor comments are presented here for further improvement of the script.

1. Introduction

(a) This statement should be referenced

"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 2oC."

(b) Line 12

Tones should be changed to tonnes

(c) Last but one line These abbreviations, NG and SGW should be defined in the text before they are presented for the first time

(2) Results and discussions

(a) Fig 1. Please correct the spelling of temperature in the box for heating rate

(b) Fig 4. The second vertical axis may be relabeled to make room for the aqueous phase

Response 3: Thank you for this observation. The manuscript has been updated accordingly.

Reviewer 4: I consider the Project "Co-pyrolysis of rice husk with underutilized biomass species" has a high research value. The copyrolysis of biomasses allows produce highly energetic materials that can replace fossil fuels, as was demonstrated in the study by the authors of the article. Studies with Malaysian biomass allow obtaining real information for the design and processing biomasses equipment, not only for the production of biofuels but also valuable chemicals.

In the article is possible to view that a rigorous methodology with high precision equipment was used, which makes evident that the results are highly reliable The method about copyrolysis of biomasses (Napier grass stem, sago biomass and rice husk) presented by the authors in this article allows to demonstrate the advantages compared to catalytic processes and multiple high-temperature reactors for the production of bio oils.

The results on the distribution of pyrolysis products and the chemical composition of the various mixtures of biomass used, allow observing the reduction of AKK (acids,

aldehydes, ketones) compared to the individual materials.

Response 4: Many thanks

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 °C, 30 °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 bio-oil yield was recorded using assorted biomass compared to pure rice husk biomass with 31.51 wt% yield. The organic phase consists 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.

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. 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 °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 [3-56]. 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 [67-89]. Studies on pyrolysis of RH to bio-oil have been carried out by many researchers [109-210].

Bio-oil yields between 25 and 38 wt% rich in acid and ketones are mostly recorded during the pyrolysis of RH at around 600 °C [12, 143, 156, 178-201]. 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 either through in-bed mixing, having biomass and catalyst in the same reactor or the use of multiple reactors with materials 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 a 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_°C, 30 °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_°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 °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-EliteTM-5ms column (30m x 0.25mm x 0.25 μ m). 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 and 6, 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 less 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. ~~The chromatogram of the analysis for the organic and aqueous phase is presented in the Figure 5 and Figure 6 respectively. The chromatograms showed similar main characteristic peaks with various intensities at retention time between 3.83 and 9.0min for the former and between 3.2 and 10.4 min for the latter.~~ This result characteristic 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 75. 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 AAK 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 57b) 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 86.

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.

Acknowledgments

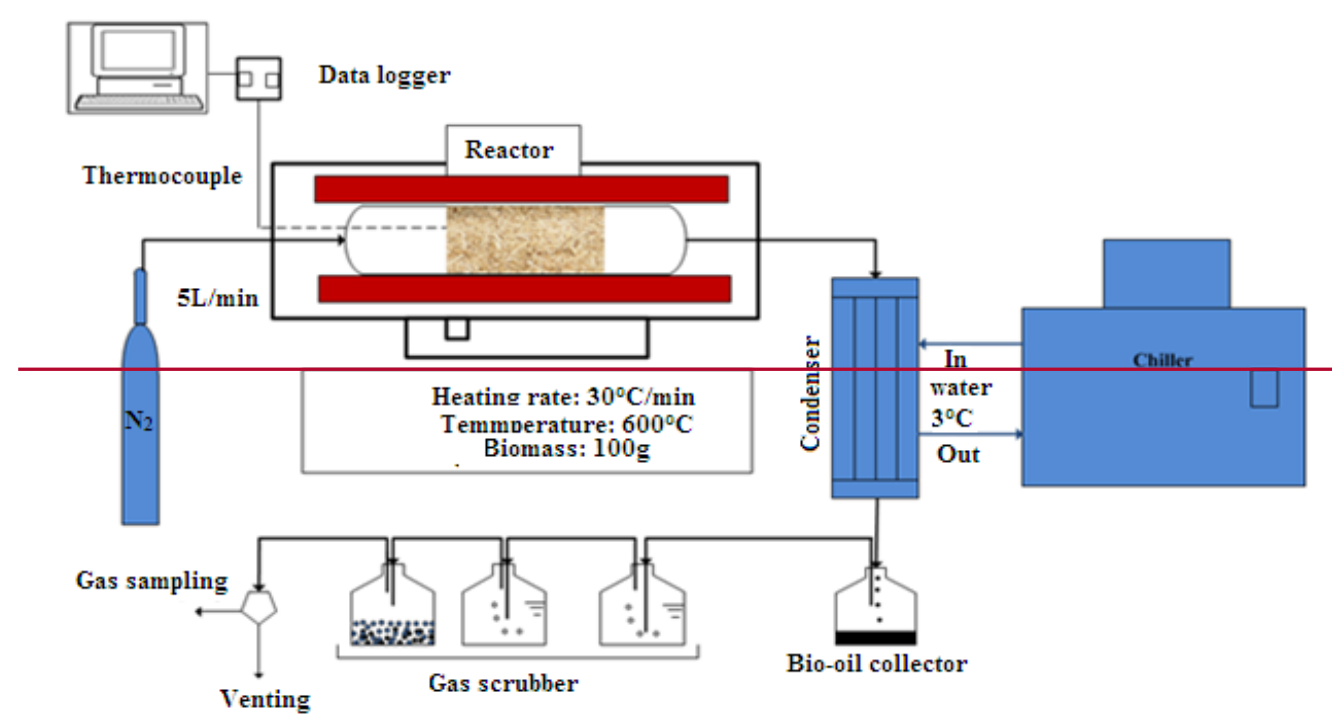
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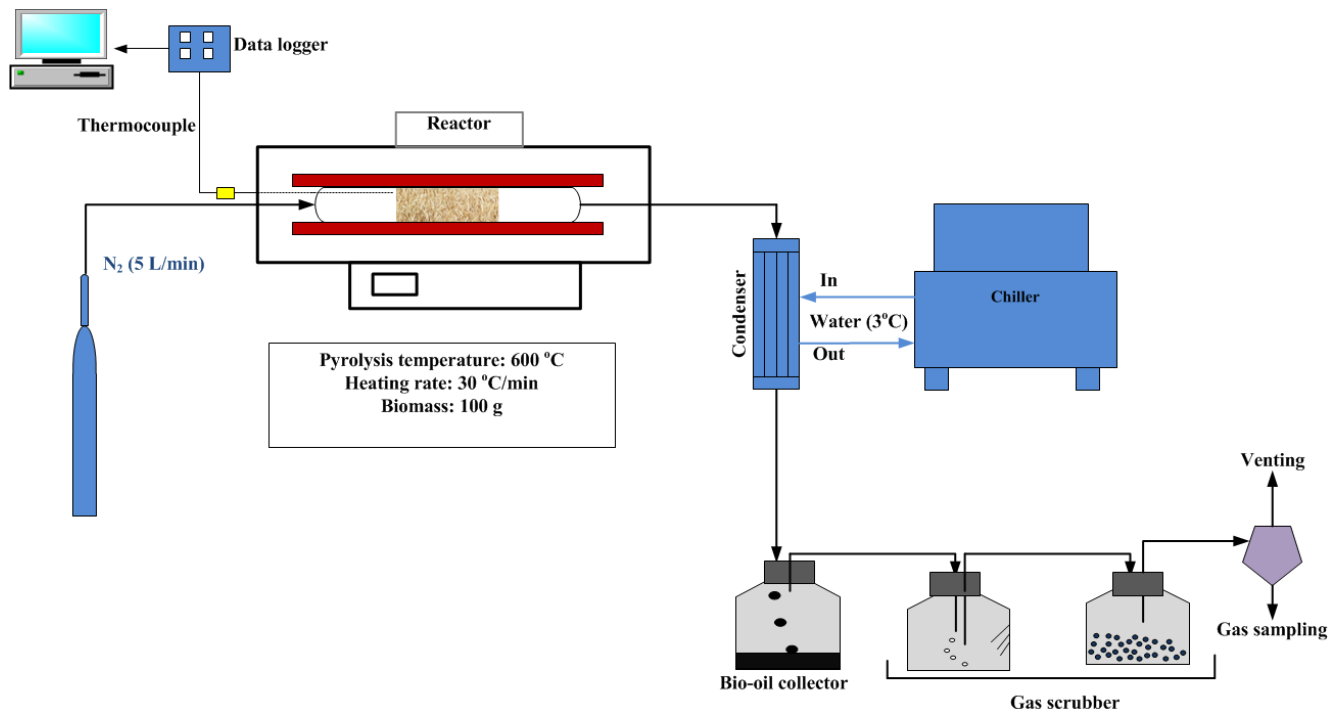
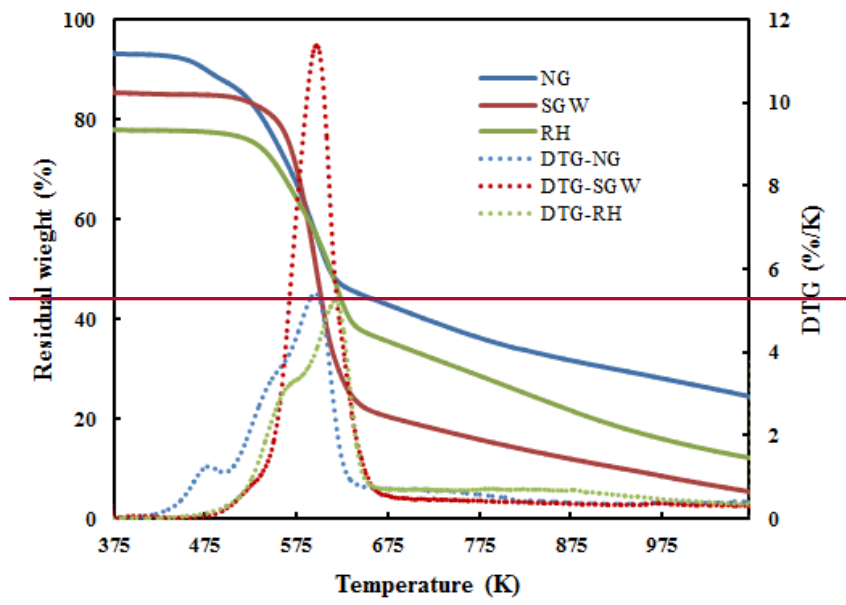


Figure 1: Schematic diagram of Pyrolysis experimental setup.



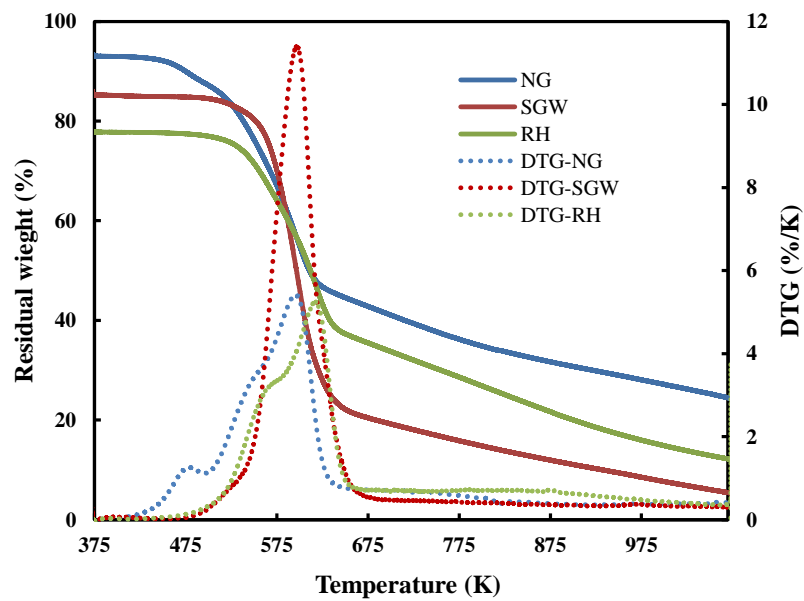
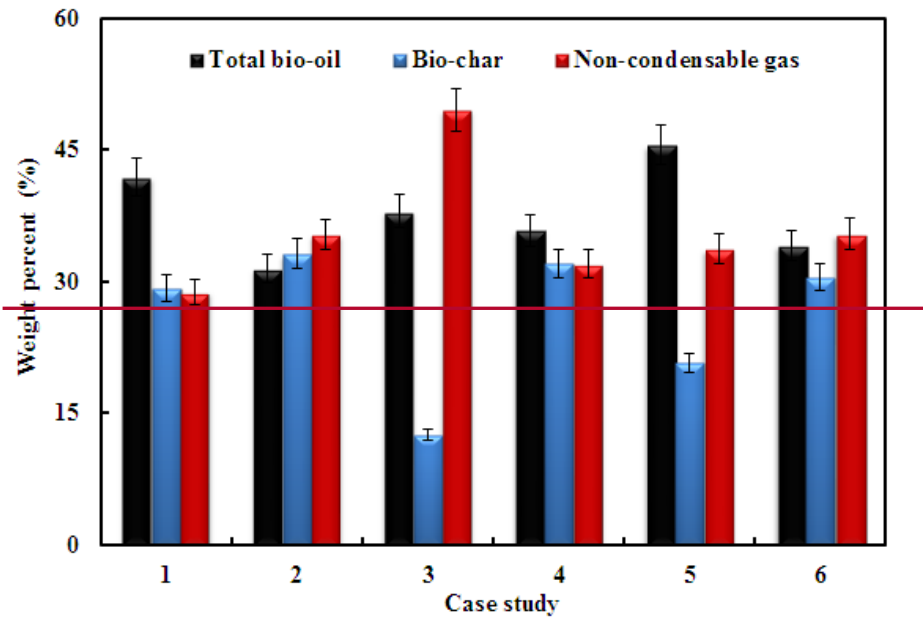


Figure 2: TG and DTG of the NG, GW and RH. Condition: nitrogen atmosphere (20 mL/min), heating rate (10 K/min).



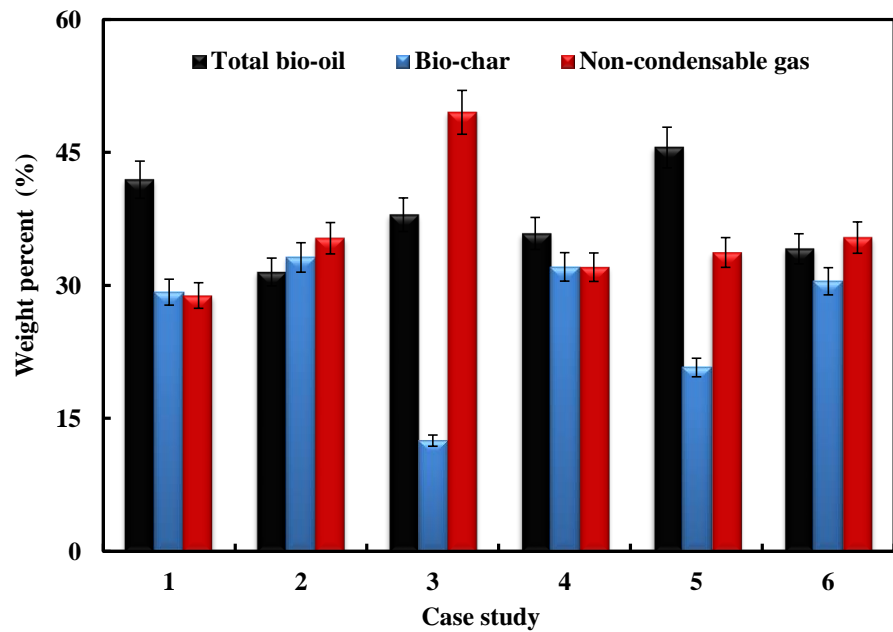
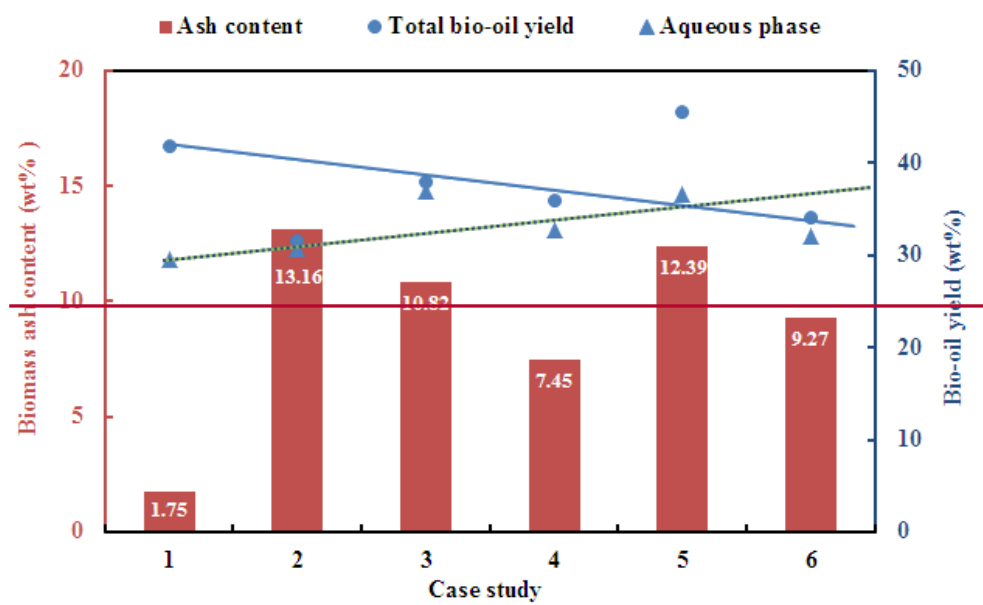


Figure 3: Pyrolysis product distribution (600 °C, 5 L/min N₂ flow and 30 °C/min heating rate). Values are the means± SD



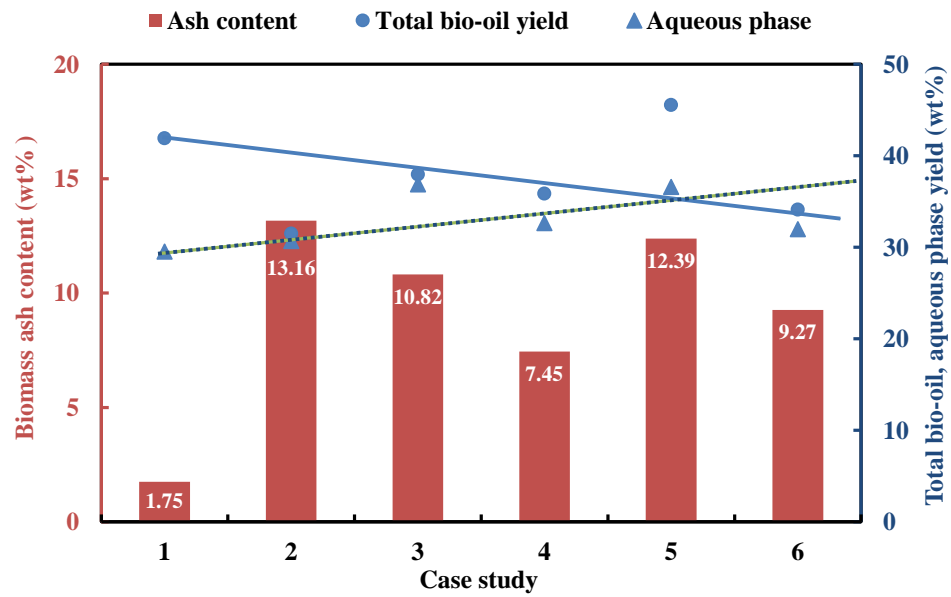
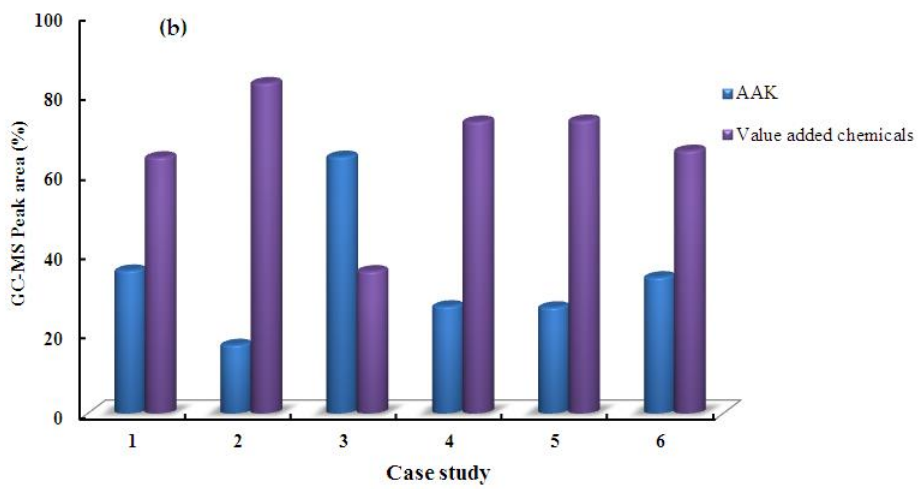
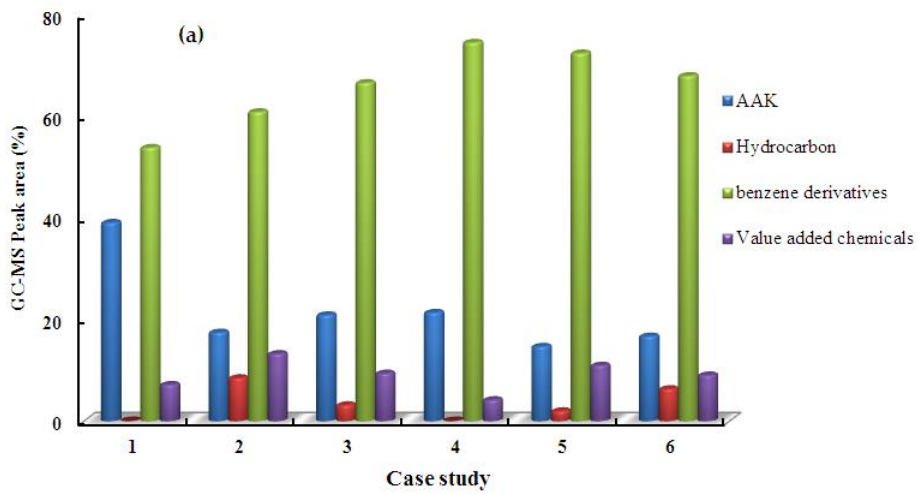


Figure 4: Relationship between biomass ash, total bio-oil yield and aqueous phase. Values are the means of three replicates



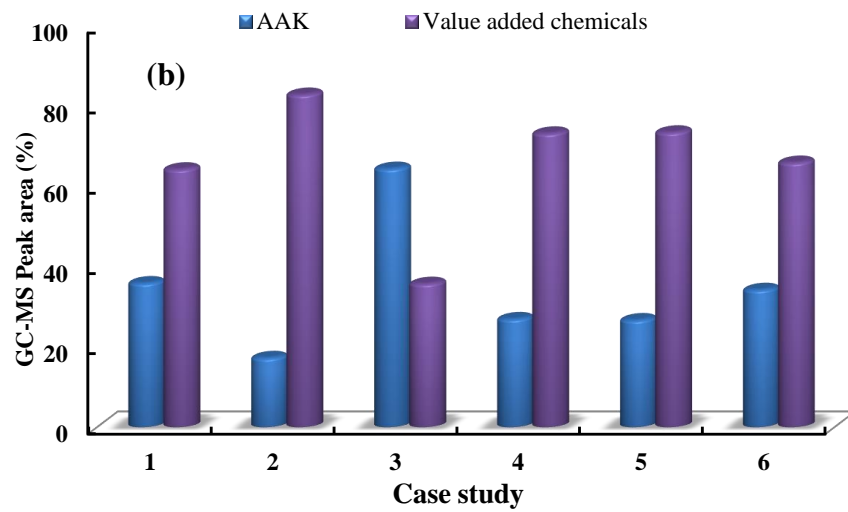
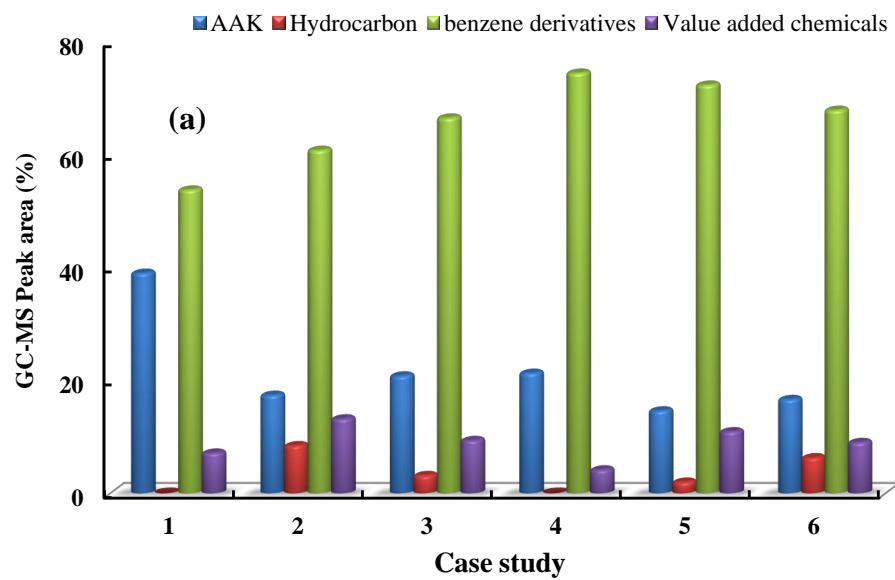
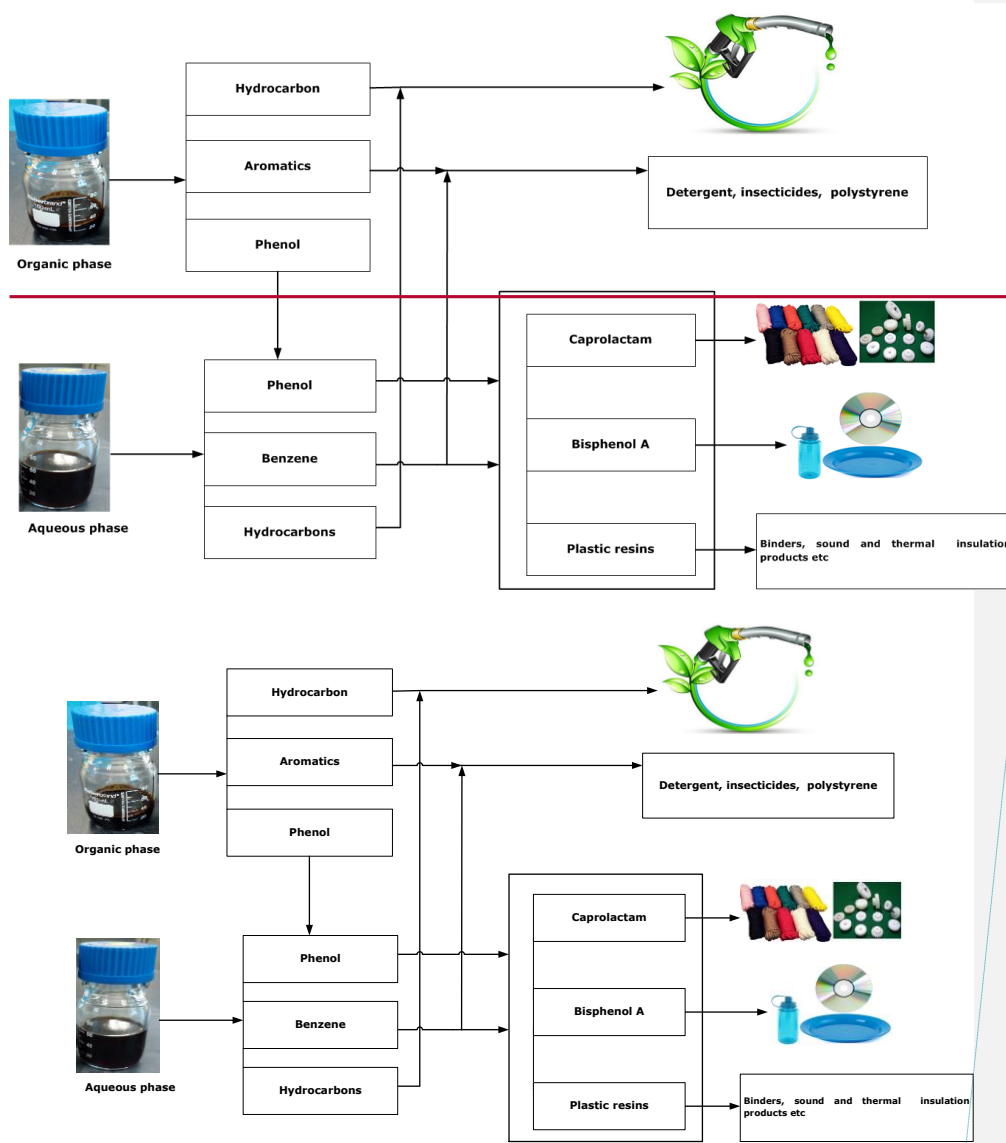


Figure 75: Groups of chemical compounds identified in the bio-oil (a) organic and (b) aqueous phase



Field Code Changed

Figure 86: Schematic diagram showing possible product that can be derived from the bio-oil

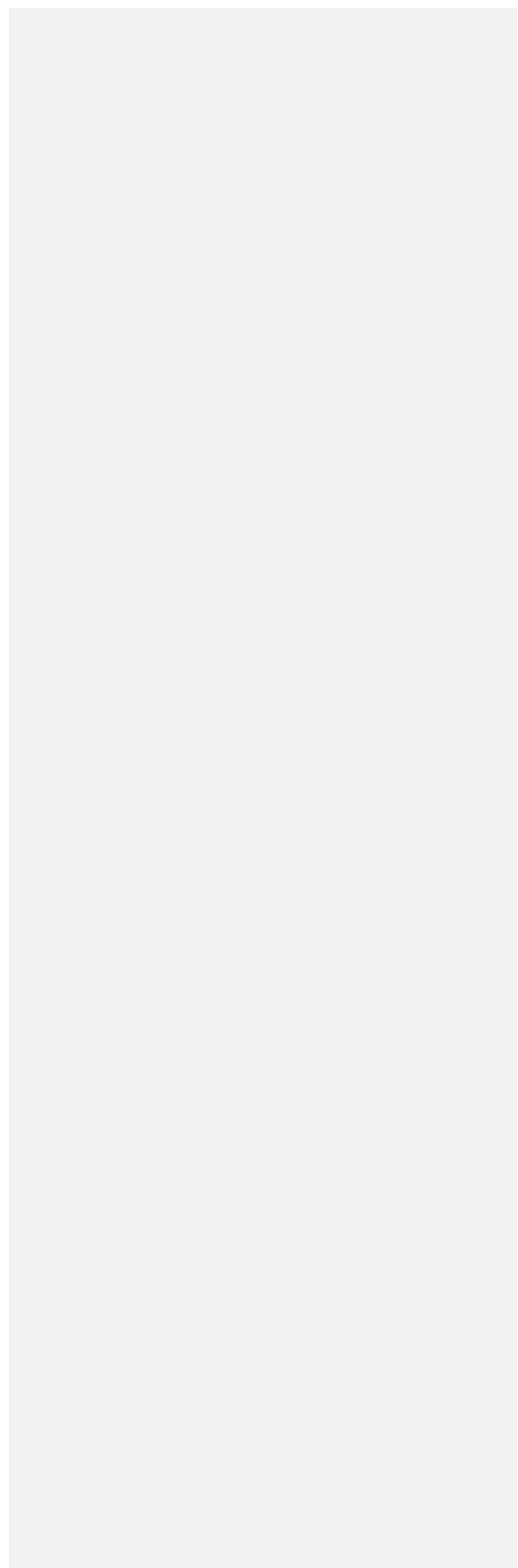


Table 1: Composition of feedstock used

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

Case study	Organic phase						H ₂ O	LHV
	C	H	N	S	O			
			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	

Case study	Aqueous phase						LHV
	C	H	N	S	O	H ₂ O	
			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 ₉ H ₁₄ O	-	-	2.81	-	-	-
3.02	3-CYCLOHEXENE-1-METHANOL, 6-HYDROXY-, CIS-	C ₇ H ₁₂ O ₂	-	-	-	1.96	-	-
3.24	CYCLOBUTENE, 2-PROPENYLIDENE-	C ₇ H ₈	-	-	3.19	2.01	-	-
3.82	BICYCLO[2.2.1]HEPTANE, 2-ETHYL-	C ₉ H ₁₆	-	-	-	-	-	-
3.82	3-FURANCARBOXYLIC ACID, METHYL ESTER	C ₆ H ₆ O ₃	-	4.29	-	3.41	-	-
3.82	FURAN, 2,5-DIMETHYL-	C ₆ H ₈ O	-	-	-	-	3.85	-
3.83	DICYCLOHEXYLMETHANOL	C ₁₃ H ₂₄ O	-	-	-	3.41	-	-
3.83	1,1-DIVINYL-1-SILACYCLOBUTANE	C ₇ H ₁₂ Si	-	-	7.36	-	-	-
3.85	L-HISTIDINE, 3-METHYL-	C ₇ H ₁₁ O ₂ N ₃	4.66	-	-	-	-	-
3.99	2-FURANMETHANOL	C ₅ H ₆ O ₂	-	-	-	-	-	-
4.03	3-FURANMETHANOL	C ₅ H ₆ O ₂	3.04	2.64	-	1.68	2.89	-
4.98	2-FURANCARBOXALDEHYDE, 5-METHYL-	C ₆ H ₆ O ₂	-	-	2.51	-	-	-
5.10	N-VINYLMIDAZOLE	C ₅ H ₆ N ₂	-	8.50	-	-	-	-
5.11	PHENOL	C ₆ H ₆ O	-	-	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 ₆ H ₈ O ₂	-	1.94	2.29	-	-	-
5.54	CYCLOHEXANONE, 5-METHYL-2-(1-METHYLETHYL)-, TRANS-	C ₁₀ H ₁₈ O	1.95	-	-	-	-	-
5.74	PHENOL, 2-METHYL-	C ₇ H ₈ O	4.05	5.14	6.77	5.14	4.48	7.27
5.90	P-CRESOL	C ₇ H ₈ O	-	8.25	7.87	7.44	6.90	-
5.93	PHENOL, 3-METHYL-	C ₇ H ₈ O	4.94	-	-	-	-	9.14
6.04	ETHANONE, 1-(1-CYCLOHEXEN-1-YL)-	C ₈ H ₁₂ O	7.62	8.58	-	-	-	-
6.04	PHENOL, 2-METHOXY-	C ₇ H ₈ O ₂	-	-	6.24	7.80	7.73	7.27
6.25	BENZALDEHYDE, 2-(2-PROPYNYLOXY)- CYCLOPENTANOL, 1,2-DIMETHYL-3-(1-METHYLETHENYL)-,	C ₁₀ H ₈ O ₂	-	-	2.03	-	-	-
6.26	[1R-(1.ALPHA.,2.BETA 1H-1,3-BENZIMIDAZOL-7-AMINE, N-[(4-	C ₁₀ H ₁₈ O	-	-	-	1.79	-	-
6.27	METHOXYPHENYL)METHYL]-2-METHYL-	C ₁₆ H ₁₇ ON ₃	1.82	-	-	-	-	-
6.49	PHENOL, 2,5-DIMETHYL-	C ₈ H ₁₀ O	2.49	3.46	4.25	3.51	3.23	6.13

6.61	PHENOL, 3-ETHYL-	C ₈ H ₁₀ O	8.17	10.15	10.09	9.95	8.37	8.20
6.83	PHENOL, 2-METHOXY-3-METHYL-	C ₈ H ₁₀ O ₂	3.67	6.15	3.48	5.52	8.98	5.31
7.01	1,2-BENZENEDIMETHANOL	C ₈ H ₁₀ O ₂	-	8.99	-	-	-	-
7.01	BENZOFURAN, 2,3-DIHYDRO-	C ₈ H ₈ O	-	-	5.77	7.45	-	3.20
7.03	BENZALDEHYDE, 2-METHYL-	C ₈ H ₈ O	13.37	-	-	-	10.08	-
7.15	PHENOL, 3-ETHYL-5-METHYL-	C ₉ H ₁₂ O	-	1.71	-	2.19	-	-
7.45	PHENOL, 4-ETHYL-2-METHOXY-	C ₉ H ₁₂ O ₂	5.37	5.68	4.68	5.85	6.34	5.37
7.71	2-METHOXY-4-VINYLPHENOL	C ₉ H 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 ₈ H ₁₀ O ₃	8.83	4.08	6.10	6.10	4.96	3.74
8.57	1,2,4-TRIMETHOXYBENZENE	C ₉ H 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 ₃ N	-	-	-	-	-	-
9.01	4-ETHYLBIPHENYL	C ₁₄ H ₁₄	-	-	-	-	-	3.24
9.05	5-TERT-BUTYLPYROGALLOL	C ₁₀ H ₁₄ O ₃	2.52	-	2.06	1.86	-	-
9.08	BENZENEAMINE, 3-ETHYL-4-HYDROXY-	C ₈ H ₁₁ ON	-	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	C ₁₃ H ₁₇ N	-	-	-	-	-	3.11
11.67	SILICIC ACID, DIETHYL BIS(TRIMETHYLSILYL) ESTER	C ₁₀ H ₂₈ O ₄ Si ₃	-	-	-	-	-	3.04
11.85	SILICIC ACID, DIETHYL BIS(TRIMETHYLSILYL) ESTER	C ₁₀ H ₂₈ O ₄ Si ₃	-	-	-	-	-	3.32
12.02	SILICIC ACID, DIETHYL BIS(TRIMETHYLSILYL) ESTER	C ₁₀ H ₂₈ O ₄ Si ₃	-	-	-	-	-	3.59
12.04	CYCLOTTRISILOXANE, HEXAMETHYL-	C ₆ H ₁₈ O ₃ Si 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 ₇ Si 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 ₆ Si ₇	-	-	-	-	2.00	-
12.37	CYCLOTTRISILOXANE, HEXAMETHYL-	C ₆ H ₁₈ O ₃ Si 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 ₇ Si ₈	-	-	-	-	-	4.17
18.97	1,4-BENZENEDICARBOXYLIC ACID, BIS(2-ETHYLHEXYL) ESTER	C ₂₄ H ₃₈ O ₄	-	-	-	-	-	-

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 ₈ H ₁₇ O ₃ N	-	-	-	-	3.50	-
3.29	PROPANOIC ACID, 1-METHYLPROPYL ESTER	C ₇ H ₁₄ O ₂	-	-	3.24	-	-	2.88
3.31	1,2,4,5-CYCLOHEXANETETROL, (1.ALPHA.,2.ALPHA.,4.ALPHA.,5.BETA.)-	C ₆ H ₁₂ O ₄	3.24	-	-	-	-	-
3.45	FORMIC ACID, 3-METHYLPENTYL ESTER	C ₇ H 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 ₇ H ₁₂ Si	-	3.91	-	-	-	-
3.82	3-(BUT-3-ENYL)-CYCLOHEXANONE	C ₁₀ H ₁₆ O	-	-	10.36	-	-	-
3.84	1H-INDENE, OCTAHYDRO-, CIS-CARBONIC ACID, 2,2,2-TRICHLOROETHYL	C ₉ H ₁₆	-	-	-	-	-	5.60
3.85	CYCLOHEXYLMETHYL ESTER	C ₁₀ H ₁₅ O ₃ Cl ₃	8.65	-	-	-	7.27	-
4.00	1H-IMIDAZOLE-2-METHANOL	C ₄ H ₆ ON 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 ₆ H ₈ O	-	-	3.64	-	-	-
4.52	CYCLOHEXENE, 3,5-DIMETHYL-	C ₈ H ₁₄	4.28	-	-	-	-	-
4.52	CARBONIC ACID, ETHYL UNDEC-10-ENYL ESTER	C ₁₄ H ₂₆ O ₃	-	-	-	3.14	-	-
4.53	2-ACETYLPYPERIDINE	C ₇ H ₁₃ ON	-	-	-	-	4.23	-
4.53	N-METHYL-3-PIPERIDINECARBOXAMIDE	C ₇ H ₁₄ ON ₂	-	2.38	-	-	-	-
4.55	2-PENTANONE, 5-(DIETHYLAMINO)-	C ₉ H ₁₉ ON	-	-	-	-	-	4.25

4.55	CYCLOPENTANONE, 2-(1-METHYLPROPYL)-	C ₉ H ₁₆ O	-	-	2.57	-	-	-
4.58	BUT-3-EN-1-YL 2-METHYLBUTANOATE	C ₉ H 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 ₈ H ₁₅ ON	-	-	4.60	-	3.02	-
4.70	UNDECANOIC ACID, 11-MERCAPTO-	C ₁₁ H ₂₂ O ₂ S	4.03	-	-	-	-	-
4.97	2-FURANCARBOXALDEHYDE, 5-METHYL-	C ₆ H ₆ O ₂	-	-	4.03	-	-	-
5.02	2-CYCLOPENTEN-1-ONE, 3-METHYL-	C ₆ H ₈ O	-	-	2.59	-	-	-
5.11	BIS(2-CHLOROETHYL) ETHER	C ₄ H ₈ OCl ₂	-	2.96	7.29	-	-	-
5.15	PHOSPHONIC ACID, (P-HYDROXYPHENYL)- 2-PROPANAMINE, N-METHYL-1-[4-[3-(1- PIPERIDYL)PROPOXY]PHENYL]-	C ₆ H ₇ O ₄ P	6.25	-	-	4.59	5.16	5.95
5.26	2,3-DIHYDRO-2-METHYL-5-ETHYLFURAN	C ₁₈ H ₃₀ ON ₂	-	-	-	-	-	4.64
5.29	2,3-DIHYDRO-2-METHYL-5-ETHYLFURAN	C ₇ H ₁₂ O	-	-	3.00	-	-	-
5.36	FURAN, TETRAHYDRO-2,5-DIMETHOXY-	C ₆ H 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 ₇ H ₈ O	-	2.09	5.47	2.67	3.22	3.30
5.90	4-IMIDAZOLACETIC ACID, BUTYL ESTER	C ₉ H ₁₄ O ₂ N ₂	-	-	4.09	-	-	-
5.91	PHENOL, 2-METHYL- (2,3-DICHLOROPHENYL)CARBAMIC ACID 4-METHOXYPHENYL ESTER	C ₇ H ₈ O	-	3.73	-	3.50	4.33	8.12
6.03	PHENOL, 2-METHOXY-	C ₁₄ H ₁₁ O ₃ NCl ₂	-	-	6.20	-	-	-
6.04	PHENOL, 2-METHOXY-	C ₇ H ₈ O ₂	-	3.29	-	4.75	5.73	6.50
6.06	IMIDAZOLE, 2-AMINOCARBONYL-1-METHYL-	C ₅ H ₇ ON 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 ₅ H ₈ Si	-	-	-	-	-	3.55
6.28	1,2,4-CYCLOPENTANETRIONE, 3-METHYL-	C ₆ H ₆ O ₃	-	-	-	-	-	3.42
6.49	4,5,6,6A-TETRAHYDRO-2(1H)-PENTALENONE	C ₈ H ₁₀ O	-	0.93	-	-	-	-
6.61	PHENOL, 2,3-DIMETHYL-	C ₈ H ₁₀ O	-	1.68	2.87	2.47	2.95	-
6.64	1,3,5-CYCLOHEPTATRIENE, 1-METHOXY-	C ₈ H ₁₀ O	4.22	-	-	-	-	-
6.83	2,3-DIMETHYLHYDROQUINONE	C ₈ H ₁₀ O ₂	-	6.02	-	-	-	-
6.83	2-CYCLOPENTEN-1-ONE, 2,3,4,5-TETRAMETHYL-	C ₉ H ₁₄ O	-	-	-	10.14	-	-
6.83	2-METHOXY-5-METHYLPHENOL	C ₈ H ₁₀ O ₂	-	-	-	-	14.09	-
6.84	PENTANOIC ACID, 2-ETHYLCYCLOHEXYL ESTER	C ₁₃ H ₂₄ O ₂	-	-	10.28	-	-	-

6.84	BENZENE, 1-ETHOXY-2-METHOXY-4-METHYL-2-PROPENAMIDE, N-(4-AMINOBTYL)-3-(3,4-DIHYDROXYPHENYL)-, (E)-	C ₁₀ H ₁₄ O ₂	-	-	-	-	-	8.22
6.91	DIHYDROXYPHENYL)-, (E)-	C ₁₃ H ₁₈ O ₃ N ₂	11.20	-	-	-	-	-
7.01	1,4:3,6-DIANHYDRO-.ALPHA.-D-GLUCOPYRANOSE	C ₆ H ₈ O ₄	-	2.53	3.77	4.11	3.04	4.42
7.04	BENZENE, (ETHENYLOXY)-	C ₈ H ₈ O	5.31	-	0.00	0.00	-	-
7.07	4-MERCAPTOPHENOL	C ₆ H ₆ OS	-	-	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 ₇ H ₈ O ₃	5.91	-	-	2.66	4.36	-
7.39	HYDROQUINONE	C ₆ H ₆ O ₂	-	-	-	-	3.35	-
7.45	4-HYDROXY-2,4,5-TRIMETHYL-2,5-CYCLOHEXADIEN-1-ONE	C ₉ H ₁₂ O ₂	-	1.29	-	-	-	-
7.45	3,4-DIHYDROXYACETOPHENONE	C ₈ H ₈ O 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 ₉ H ₁₀ O ₄	-	2.76	-	-	-	-
7.96	PHENOL, 2,6-DIMETHOXY-	C ₈ H ₁₀ O ₃	9.14	-	5.86	3.45	5.14	5.43
8.56	PHENOL, 4-METHOXY-3-(METHOXYMETHYL)-	C ₉ H 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 ₆ H 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)-.ALPHA.-D-GLUCOPYRANOSE, 4-O-.BETA.-D-	C ₁₀ H ₁₂ O ₃	2.51	1.47	-	-	2.75	-
9.19	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	-	-	-	-	-