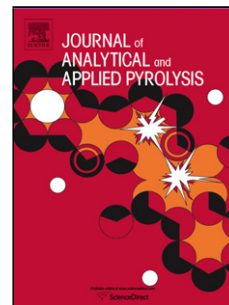


## Accepted Manuscript

Title: Increased charcoal yield and production of lighter oils from the slow pyrolysis of biomass

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PII: S0165-2370(16)30598-8  
DOI: <http://dx.doi.org/doi:10.1016/j.jaap.2017.01.028>  
Reference: JAAP 3953

To appear in: *J. Anal. Appl. Pyrolysis*

Received date: 28-9-2016  
Revised date: 6-12-2016  
Accepted date: 27-1-2017

Please cite this article as: S. Russell, J.L. Turrion-Gomez, W. Meredith, P. Langston, C.E. Snape, Increased charcoal yield and production of lighter oils from the slow pyrolysis of biomass, *Journal of Analytical and Applied Pyrolysis* (2017), <http://dx.doi.org/10.1016/j.jaap.2017.01.028>

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# 1 Increased charcoal yield & production of lighter oils from the slow pyrolysis of biomass

2  
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## 9 10 Highlights

- 11
- 12 • Grey King Slow Pyrolysis was performed on pinewood with bentonite addition over 400-700C
- 13 • Clay addition showed increasing decomposition of heavy pyrolysis oils, into lighter oils, coke and gas
- 14 • Cracking caused by clay produced lower molecular weight compounds of lighter oils

## 15 16 Abstract

17  
18 In an effort to reduce CO<sub>2</sub> emissions from solid fuels, a considerable amount of research is going into how  
19 improve the manufacturing processes and product properties of the products from pyrolysis. One aspect that  
20 is often overlooked is the production of charcoal for cooking and soil remediation, which is an inefficient  
21 conversion process. There is considerable interest into using additives to increase charcoal yields, and  
22 based on the observation from fast pyrolysis work that certain catalyst tar cracking pathways can deposit  
23 considerable amounts of coke on the surface of the catalyst, there is a potential application to slow pyrolysis  
24 processes producing charcoal. Alumino-silicate catalysts have been shown to have a relatively high  
25 tendency to do this. This work hypothesises that this catalysation can be applied to slow pyrolysis, with low  
26 cost alumino-silicate minerals, specially bentonite clay, which has been added to pine pyrolysis in  
27 concentrations up to 60% wt (against input biomass) at temperatures 300 – 700°C.

28  
29 This study has shown that the use of bentonite clay minerals can be beneficial to the process, as there is an  
30 increase in the charcoal yield from biomass, whilst the proximate analysis of the charcoal shows little change  
31 from levels expected from biomass only pyrolysis. The conversion of oil to charcoal was more effective at  
32 high temperatures due to higher levels of oil cracking. At 700°C with 60% clay loading, charcoal yield  
33 increased 16%wt (dry ash free basis) was seen, while at the same time 19% extra gas was produced at the  
34 expense of 35% of the oil from raw pine pyrolysis. This indicates fuel properties of the charcoal are  
35 predictable, and changes in yield considerable. At the same time, the abundance of lower molecular weight  
36 oils is increased (relative to 4-methyl phenol). It is thought that pyrolysis oil reacts with the clay, causing the  
37 heavier tars to disproportionate into charcoal and gas.

## 38 39 Keywords

40  
41 Slow Pyrolysis; Biomass; Clay Minerals; Catalyst; Charcoal; Oil

42

## 43 1 Introduction

44

45 Production of heating fuels to compete with conventional fossil fuels (gas, oil and coal) has become a priority  
46 for countries following the Paris Climate Change Agreement that sets out limits on the targeted global  
47 temperature rise. For fulfilment of this agreement, energy sources and feedstocks are going to need to be  
48 better utilised, one of these being abundant agricultural wastes and residues [1]. In the context of Europe, if  
49 used correctly, agricultural wastes and forestry residue can offer a sustainable solution to part of the future  
50 fuel scenarios, crucially having the ability to provide oil and solid fuel, as well as gas which can be utilised for  
51 electricity, where as many other systems (hydro, solar, wind, tidal etc.) can only directly produce electricity.

52

53 One technology that can utilise these biomass types is pyrolysis. This has been used with several levels of  
54 technological intensity to produce charcoal for soil amendment and cooking to oil and fine chemicals for  
55 centuries [2, 3]. Charcoal use is still widely employed today for domestic cooking, as it is a more consistent,  
56 cleaner burning product with higher energy density than raw biomass. There is also a reduction in smoke  
57 output due to the increased fixed carbon content [4-6]. Cha, et al. [7] have reviewed more modern uses of  
58 charcoal, which range from soil amendment for increased fertility and carbon sequestration to replacement of  
59 fossil fuel absorbents. These areas outline that charcoal production is important, but conversion efficiency of  
60 biomass processes are quite low due to the reaction thermodynamics [8]. Greater recovery of biomass as  
61 charcoal could lower the cost of production for these applications which is the purpose of this study.

62

63 Many studies have investigated how to increase this conversion through modifying the process conditions  
64 and with use of additive in the pyrolysis, particularly through the use of alkaline/alkali earth metals, transition  
65 metal oxides and alumino silicates such as zeolite and clay minerals.

66

67 Generally, the most important process condition to modify in order to increase the charcoal yield is to lower  
68 peak pyrolysis temperature [9] because lower levels of volatile compounds are released as gas and tar.  
69 Increases in charcoal yield can also be made by controlling the heating rate – decreasing heating rates  
70 mean that there is a longer residence time of volatile compounds in the fixed carbon structure, so more of  
71 these volatiles are fixed and retained [10, 11]. Pre-drying of the biomass so that moisture removal does not  
72 strip volatile matter and increasing the vapour phase residence time to allow for more secondary tar  
73 conversion to charcoal [3] are also well known techniques to increase charcoal yield. Aside from temperature  
74 however, the most promising operating conditions to increase charcoal yield are to increase operational  
75 pressure [3, 12] and increase the particle size [13]. The issue with these systems is that they require good  
76 process control and high capital cost equipment, and cannot be retrofitted to current production systems  
77 cheaply. Large biomass particles also generally require the use of virgin wood stocks, rather than chips or  
78 pellets which can utilise waste.

79

80 Heating rate and residence time are also broken into two characteristic types of pyrolysis; fast pyrolysis  
81 systems (residence time = 10-20 sec, high heating rate [14]), or slow pyrolysis (residence time = 5 – 30  
82 mins, low heating rate [14]) has a great effect on the yield outcomes. Slow pyrolysis is conventionally used to  
83 produce charcoal and has been the basis of this study, however, much literature exists on additive fast  
84 pyrolysis.

85  
86 Fast pyrolysis systems generally exist to produce gas and oil from biomass, however the pyrolysis process  
87 produces gas and oil with relatively poor quality compared with conventional fossil fuels [2], with  
88 considerable refining required to improve these products [15]. In situ catalysation has been extensively  
89 studied using: impregnated or raw zeolites or similar low cost alumino-silicate materials clay minerals;  
90 increasing the level of natural atomic earth metals (generally acidic, e.g. K, Ca) or adding generally basic  
91 transition metal oxides (e.g. MgO) [16-21]. These are added to the pyrolysis reactor with the aim of cracking  
92 heavy oils in the oil, reducing the amount of oxygenation present in the resulting oil, or changing the resulting  
93 pyrolysis product mixture. Each of these systems impact the pyrolysis in a different way; minerals and  
94 zeolites generally involve reactions in the gas phase, between the de-volatilised compounds and the catalyst;  
95 while atomic earth metal addition can be of great effect to changing how the lignin and cellulose interact and  
96 decompose. The issue with metal addition to the pyrolysis is that it limits the use of the final charcoal  
97 potentially due to remaining toxicity from the metals. Therefore, this study will investigate mineral catalysis.

98  
99 Alumino-silicate minerals and zeolites that have a high concentration of Lewis acid sites, relatively high  
100 surface area and mesopores and have been identified in the literature as increasing cracking [22-27]. These  
101 cracking reactions are a wide mixture of dehydration reactions which break down and decarboxylate the ring  
102 structures present in the oils [28]. Studies have shown that zeolites can produce higher concentration of  
103 valuable aromatic compounds than non-catalytic runs too opening up the potential of investigation of  
104 specialty chemical refining from the process [29]. If the decomposition products are not small enough to be  
105 released as gas, then fouling of the catalyst can occur as the fragments recombine and deposit on the  
106 surface as coke. In the case of this study, this is being considered as extra char yield, as it is assumed that  
107 this will behave as charcoal.

108  
109 Rutkowski [30] and Solak and Rutkowski [31] have looked into applying these effects to fast pyrolysis of  
110 plastic wastes with several types of clay mineral (montmorillonite and bentonite) under fast pyrolysis  
111 conditions. They found oil quality was improved but yield was reduced, as oil was cracked into gas and coke  
112 which fouled the catalyst. High coke deposits were observed, especially using bentonite. From these studies,  
113 it appears that bentonite could be promising for the purposes of this work on biomass.

114  
115 Some groups have already looked at applying these concepts to slow pyrolysis. For example Veses, et al.  
116 [16], Gerçel [32] showed that slow pyrolysis systems can be modified in a similar way using the mineral  
117 sepiolite, which can mimic the properties of basic transition metal oxides, while other studies have showed  
118 that atomic earth metal addition can also applied to slow pyrolysis [16, 33]. Gerçel [32] also showed findings  
119 that agreed with Rutkowski [30] that sepiolite lowers the yield of charcoal, so it could be expected that the  
120 effects using bentonite may translate to slow pyrolysis as well. Bentonite was looked at by Veses, et al. [19],  
121 who studied the effects of it at 450°C. This study provides evidence that with pinewood liquid yield is reduced  
122 and tar cracking reactions are happening, but have not characterised the results over a temperature range or  
123 catalyst concentration as they have done with sepiolite.

124  
125 The aim of this work is to see the effect that the addition clay mineral bentonite has on the extent of tar  
126 disproportionation into lower molecular weight oils, coke and gas as well as providing composition data on

127 the oils obtained and showing how the composition simplifies with increasing clay concentration from slow  
128 pyrolysis of pinewood. This will be done over a temperature range from 400-700°C and clay mineral  
129 concentrations of up to 60%wt (compared to input biomass), a much greater range than presented in Veses,  
130 et al. [19]. Pinewood has been chosen for its abundance in European and American forests and its widely  
131 studied nature. It was hypothesised that the higher addition of clay mineral would produce higher charcoal  
132 yields due to the solid acid catalyst nature of the material; with the added benefit of better quality gas and  
133 lower molecular weight chemicals.

134

## 135 2 Materials and methods

136

### 137 2.1 Materials

138

139 Pinewood chips, sourced from a commercial supplier for home boilers in the UK (Forest Fuels), were ground  
140 to pass through a 3 mm screen. Proximate analysis moisture (ASTM D2016), volatile matter (ASTM E872-  
141 82) and ash (ASTM D1102-84) of this biomass shows it has the composition Volatiles = 86.1%wt,dry; Ash =  
142 0.6%wt,dry; Moisture = 15.2% as received (ar).

143

144 The clay used for these experiments was laboratory grade powdered clay (Fullers Earth - Sigma Aldrich,  
145 montmorillonite clay with similar structure and functionality to bentonite clays mentioned above, able to pass  
146 through a 0.149 mm mesh). 10g of these components were mixed in a beaker in proportions from 0 to 100  
147 %wt clay, so extent of clay chemical moisture loss at the experiment temperature could be observed. This  
148 mixture was then transferred to a quartz retort tube and placed in a horizontal tube furnace (HTF), and setup  
149 as a Gray-King assay, as shown in

150 Figure 1. This is has been developed as a method to characterise coal [34], but has been used here to get a  
151 simple carbonisation of the biomass, mimicking many 'low tech' carbonisation plants where there is no  
152 nitrogen or inert gas inlet.

153

154 A control experiment has also been performed using sand to determine if effects seen are due to clay/liquid  
155 reactions or simply a physical blocking of biomass pores. Sand (generic kiln dried paving sand), clay and  
156 pinewood mixtures were made to match the equivalent clay to pinewood mixtures in the main study. To do  
157 this, a 10 g mixture using 4 g of pinewood was made and the concentration of sand and clay varied to match  
158 the mixture requirements.

159

### 160 2.2 Pyrolysis system

161

162 Grey-King pyrolysis occurred in a sealed quartz tube inside the HTF. No carrier or sweep gas was used. Gas  
163 and liquid products escaped due to natural flow from a side arm into a round bottom flask in an ice water  
164 bath. Liquid products were collected by condensation in a round bottom flask in an ice bath, while non  
165 condensable fractions were collected a gas bag.

166

167 The HTF was pre-heated to 250°C to prevent effects on uncontrolled heating due to the furnace setup, then  
168 the biomass sample was introduced and heated to peak temperatures of 400, 500 and 700°C at a heating

169 rate of 20°C/min. Dwell time at the peak temperature was 1 hour. The sand/clay/pinewood experiment was  
170 only carried out at 500°C only.

171  
172 The charcoal was left to cool in the furnace until below 300°C, when the quartz tube was removed for natural  
173 cooling. Pyrolytic liquid (oil and water mixture) and charcoal collected were weighted for yield, then  
174 characterised. Product yields was calculated on a dry clay and ash free basis, taking into account the  
175 chemical moisture lost from the clay at the various heating temperatures. Gas yield was calculated by  
176 difference. Characterisation on the liquid products was only carried out on one set of experiments, but  
177 several repeats of the yield experiment have been conducted.

### 178 179 2.3 Charcoal characterisation

180  
181 Charcoal and clay were not separated, but were mixed and ground in a pestle and mortar until a fine powder.  
182 The mixture was then subject to proximate analysis as described above. Samples of raw clay were also  
183 subject to pyrolysis, and the proximate analysis of this performed which allowed calculation of the dry ash  
184 free volatiles content of the pinewood charcoal.

### 185 186 2.4 Liquid characterisation

187  
188 Samples of the liquid were used for two analysis types:  
189 

- Gas Chromatography Mass Spectrometry (GC-MS) analysis for composition determination.  
190 Approximately 0.5 ml of sample was removed and used for this analysis
- Dean-Stark titration to determine water content. Remaining sample was mixed with toluene and  
191 titrated until water collection volume was stable.

### 192 193 194 2.5 GC-MS analysis

195  
196 Oil samples were weighed into a sample tube and diluted with dichloromethane. GC-MS in full scan mode  
197 ( $m/z$  40-450) was performed on the samples with a Varian CP-3800 gas chromatograph, interfaced to a  
198 Varian 1200 mass spectrometer (EI mode, 70 eV). Separation was made using a ZB-1701 fused silica  
199 capillary column (60 m x 0.25 mm i.d., 0.25 mm thickness), with helium as the carrier gas, and an oven  
200 programme of 50°C (hold for 2 min) to 300°C (hold for 33 min) at 5°C/min. GC-MS output covers the range  
201 up to number of carbon atoms (NC) 35.

202  
203 The chromatograms were then split into heavy and light fractions based on the retention time of 4 methyl  
204 phenol (boiling point 201°C, molecular weight 108.13g/mol, approximately NC-13). The relative peak area  
205 before and after this compound were then compared to get a qualitative measure of oil cracking.

## 206 207 3 Results and discussion

### 208 209 3.1 Changes in the system mass balance with clay addition

210

211 Figure 2 and Figure 3 present the pyrolysis yield breakdown on a dry (relative to raw) biomass ash free, clay  
212 free basis (as clay provides mostly ash, this is referred to as dry ash free basis (DAF)). These two figures  
213 show a reduction in oil yield, which causes an increase in charcoal and gas yield, although at 700°C there is  
214 some water loss which could be due to favoured gas phase reactions utilising the water, under steam  
215 reforming pathways [35]. Parallels with the 1:6 weight ratio (16.7 wt%) bentonite 450°C experiment by  
216 Veses, et al. [19] can be seen by interpolating between the 400 and 500°C experiments in this study,  
217 indicating some agreement between the works.

218  
219 Plotting these charts to show the difference in yield with non-catalysed pyrolysis (Figure 4), highlights how  
220 these changes in conversion preference are occurring and shows that the main driver for the reaction to  
221 change is temperature. Figure 2B and 4B compare the charcoal yield in a system using sand, i.e. extra inert  
222 material, as well as the clay. This shows that there is a little difference in the level of extra charcoal  
223 production when sand is added to the system, indicating secondary char formation due to pore blocking or  
224 physical oil interaction with solid particles is relatively low. This observation provides evidence that the  
225 reaction presented is an effect of the solid acid catalyst properties of the clay. The absolute extent of the oil  
226 conversion to extra charcoal may be influenced by factors not studied as part of this set of experiments  
227 aiming to determine the fundamental concept that clay catalyst can be used in context. The main factor that  
228 could effect this is volatile residence time post pyrolysis (which is relatively high in the case of Grey-King  
229 pyrolysis where no sweep gas is used), and contact of volatiles with the clay and charcoal post volatilisation.  
230 At lower temperatures, the conversion of oil to charcoal is favoured, while at higher temperature the  
231 conversion to gas is preferred. Due to the nature of the clay mineral and findings from literature, it is  
232 speculated that these results are showing catalytic cracking of the liquid into the charcoal and gas products,  
233 which is expected to become more efficient at higher temperatures as gas phase cracking become more  
234 dominant [19, 35]. There may be some evidence in the data that low concentrations of clay experience some  
235 inactivation due to blocking of active site by charcoal condensation on the clay surface, but further  
236 experiments are required to determine the full extent of the clay's activity.

237

### 238 3.2 Changes in product streams quality

239

#### 240 3.2.1 Effect of clay addition on charcoal quality

241

242 As the clay and charcoal were not separated, the effect the clay has on the charcoal quality was estimated  
243 by determining if there were any differences between the calculated volatiles content and the content  
244 measured experimentally (Figure 5) by subtracting the volatiles from the clay. As can be seen, there are no  
245 adverse effects, i.e, significant change in volatiles, from the addition of clay to the experiments. Therefore it  
246 is assumed that charcoal quality is not affected by clay addition.

247

#### 248 3.2.2 Effect of clay addition on oil composition

249

250 Figure 6A presents the GC-MS analysis of the liquid stream for 0, 30% and 60% clay concentration  
251 experiments at 500°C, to highlight the oil composition changes with clay concentration and Figure 6B shows  
252 the temperature effects from 500 – 700°C, at 60% clay concentration. Figure 7 breaks these streams down

253 into heavy and light fractions, and shows that there is a significant cracking effect as light fraction increases  
254 from approximately 50% to around 80% of the total oils in the sample. From these plots, it can be seen there  
255 is considerable effect on the composition of the oil via the addition of clay. Figure 7 also indicates that there  
256 is some increase in the cracking effect by increasing temperature, as expected [9, 22] from previous studies  
257 but in terms of the relative cracking effect, increasing temperature only increases the total amount of oil  
258 cracked.

259  
260 These observations, with the loss of oil and gain in charcoal are evidence that there is a temperature and  
261 clay dependent cracking reaction occurring. This is causing the breakdown of heavy oils from the biomass  
262 pyrolysis and having the effect of improving the oil, potentially drastically lowering the cost of refining before  
263 sale or increasing heating value. More charcoal is also produced, which it is assumed could either be burnt  
264 off to regenerate the clay, or utilised as the clay/charcoal mixture in some manner, but future work would be  
265 needed to see the effect this would have on the heat content of the clay/charcoal, and determine the effects  
266 on the quality of the gas produced. Studies are also required to look into the effects of recycling the clay to  
267 see if there are any issues with its re-use following combustion of the resulting clay; and to see what specific  
268 chemicals or fuels can be extracted from the resulting oil.

269

#### 270 4 Conclusions

271

- 272 • Clay mineral bentonite addition led to the improvement of the charcoal and gas yield at the expense  
273 of heavy oils during biomass pyrolysis. Future work should be carried out to determine how best the  
274 clay charcoal mixture can be utilised for soil amendment or combustion.
- 275 • Improvement in the remaining oils following clay addition with lighter fractions becoming more  
276 dominant
- 277 • Increasing pyrolysis temperature and clay mineral content lead to a greater degree of the mentioned  
278 reaction. Again, further experiments are required to quantify the full extent of the clay oil reaction.
- 279 • Findings agree with and extend on other literature in the area.

280

#### 281 Acknowledgements

282

283 Thank you to the ESPRC for the funding for the Efficient Fossil Fuels Technology Doctoral Training Centre  
284 through grant EP/G 037345/1 and CPL Industries Ltd. for providing financial support for this project.

285

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287

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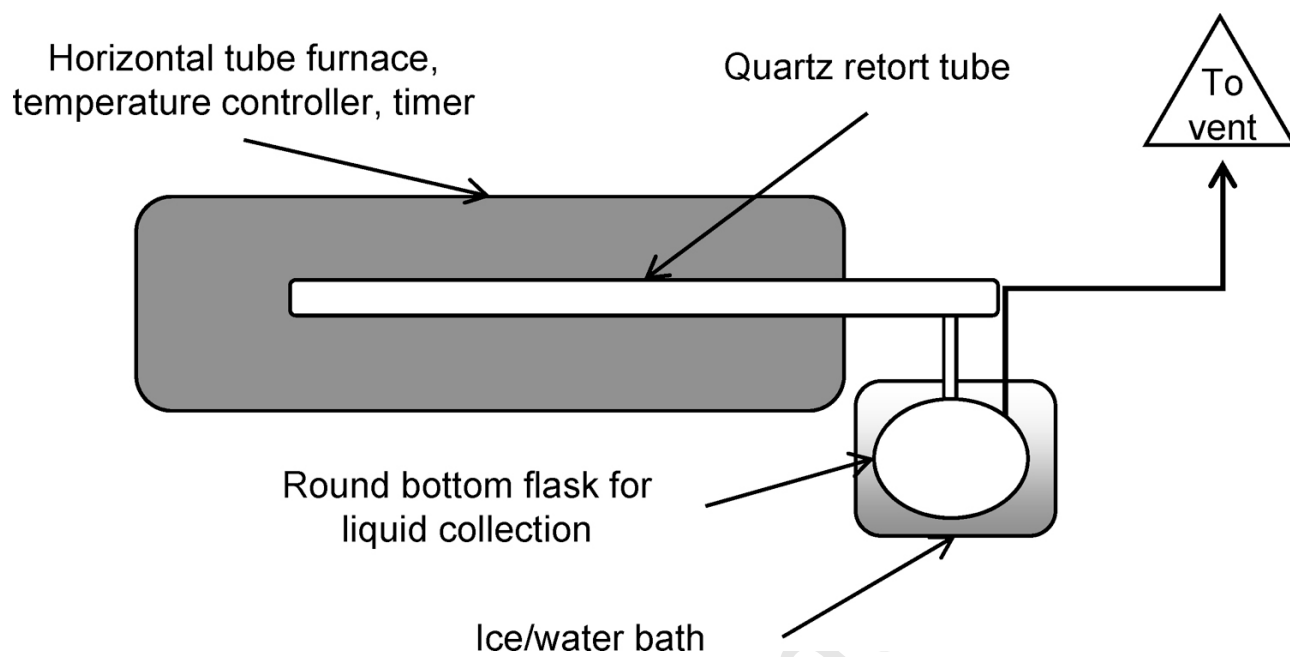


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362 List of captions  
363  
364 Figure 1. Setup of Gray King pyrolysis assay. Biomass and clay are loaded into the quartz retort tube and  
365 heated with the horizontal furnace.  
366  
367 Figure 2. Gas, solid and liquid phase yields of pine wood at 400°C (2A), 500°C (2B), 700°C with 6  
368 concentrations of clay (0, 10, 20, 30, 40, and 60 (%wt). Gas yield is calculated by difference.  
369  
370 Figure 3 Changes in oil/pyrolytic water breakdown of liquid phase produced during pyrolysis at 400°C (3A),  
371 500°C (3B) and 700°C (3C).  
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373 Figure 4. Change in product yields relative to no catalyst pyrolysis, dry ash free basis, at 400°C (3A), 500°C  
374 (3B) and 700°C (3C).  
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376 Figure 5. Volatile content of charcoal produced by pyrolysis, dry ash free basis.  
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378 Figure 6 Total ion chromatograms from the GC-MS of oils from pyrolysis: Plot 7A. Constant temperature,  
379 500°C increasing clay concentration, 0 -60 wt% and Plot 7B. Constant clay concentration, 60 wt%, and  
380 increasing temperature 500 – 700°C. Arrows above the chart are indicating heavy and light oil fractions.  
381 Peak assignments: 1. furfural 2. 2 methyl cyclopent-1-one, 3. 1,2 cyclopentadiene, 4. 5 methyl furan  
382 carboxaldehyde, 5. 2-furanone, 6. 5 methyl furanone, 7. 2 hydroxy 3 methyl 2 cyclopent-1-one, 8. phenol, 9.  
383 2 methoxy phenol, 10. 2 methyl phenol, 11. 3 methyl phenol, 12. 4 methyl phenol, 13. 2 methoxy 4 methyl  
384 phenol, 14. 4 ethyl 2 methoxy phenol, 15. Dianhydro glucopyranose, 16. eugenol, 17. 2 methoxy 4 propenyl  
385 phenol, 18. vanillin, 19. Hydroxy methoxy phenol 2 ethanone, 20. Hydroxy methoxy phenol 2 propanone.  
386  
387 Figure 7. Effect of clay concentration and temperature on fraction of light oils produced by pyrolysis.  
388 Distinction between heavy and light oil based on retention time above that of 4-methyl phenol; BP of 201°C,  
389 molecular weight, 108.13g/mol.  
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391 Figure 1

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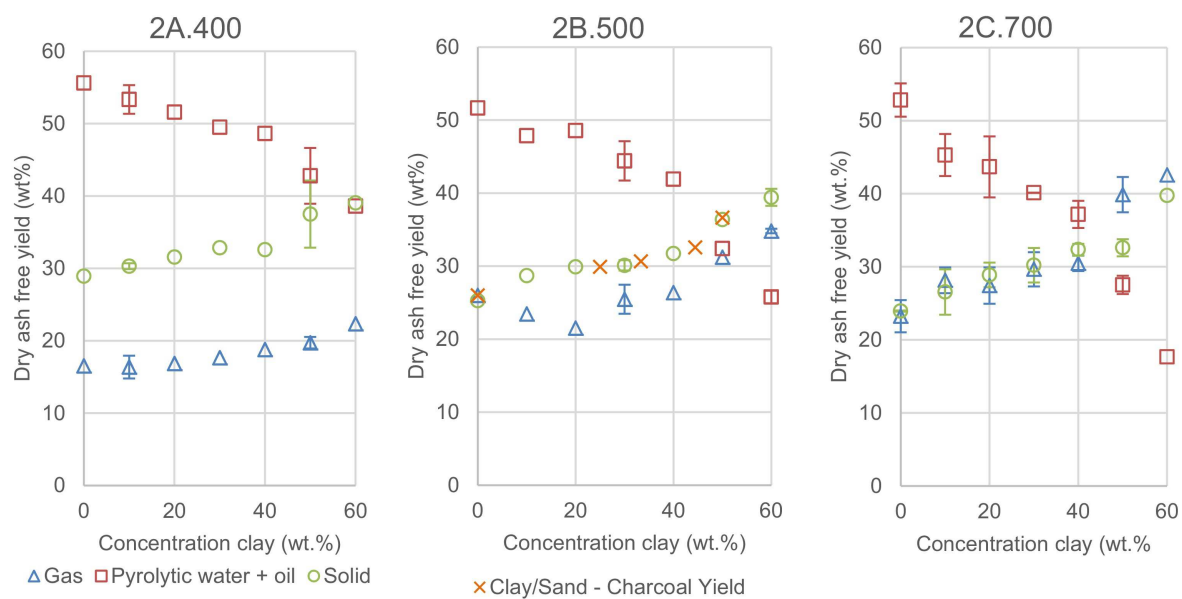


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394 Figure 2

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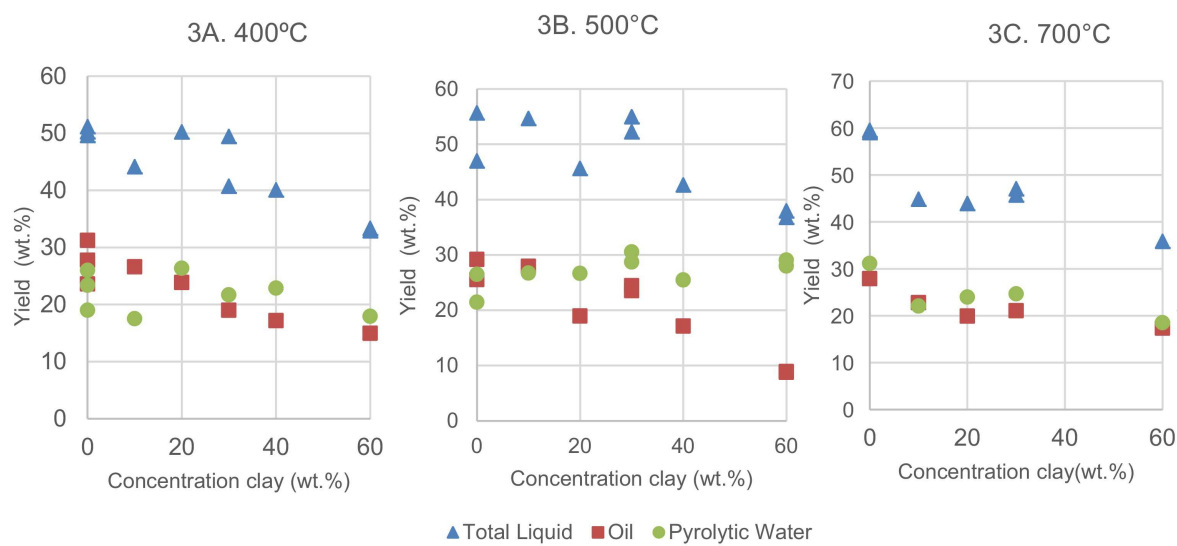
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399 Figure 3

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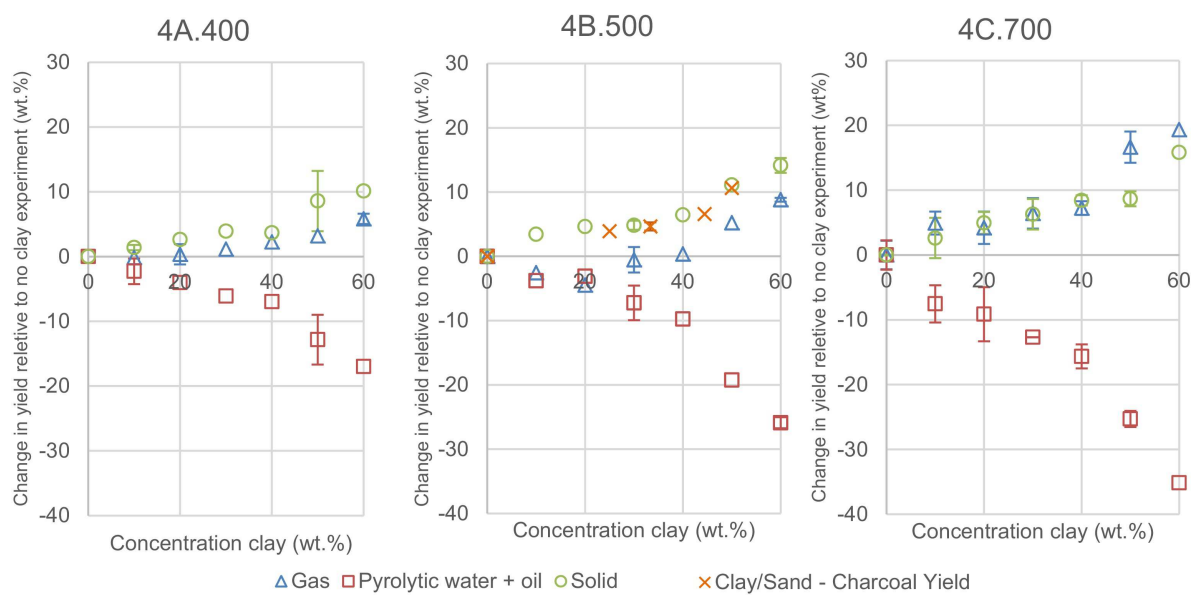
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403 Figure 4

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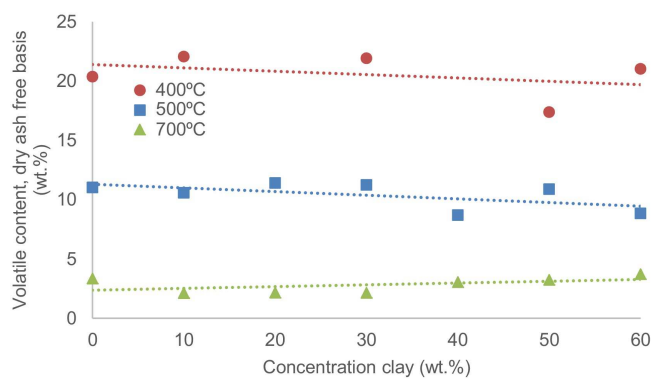
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407 Figure 5

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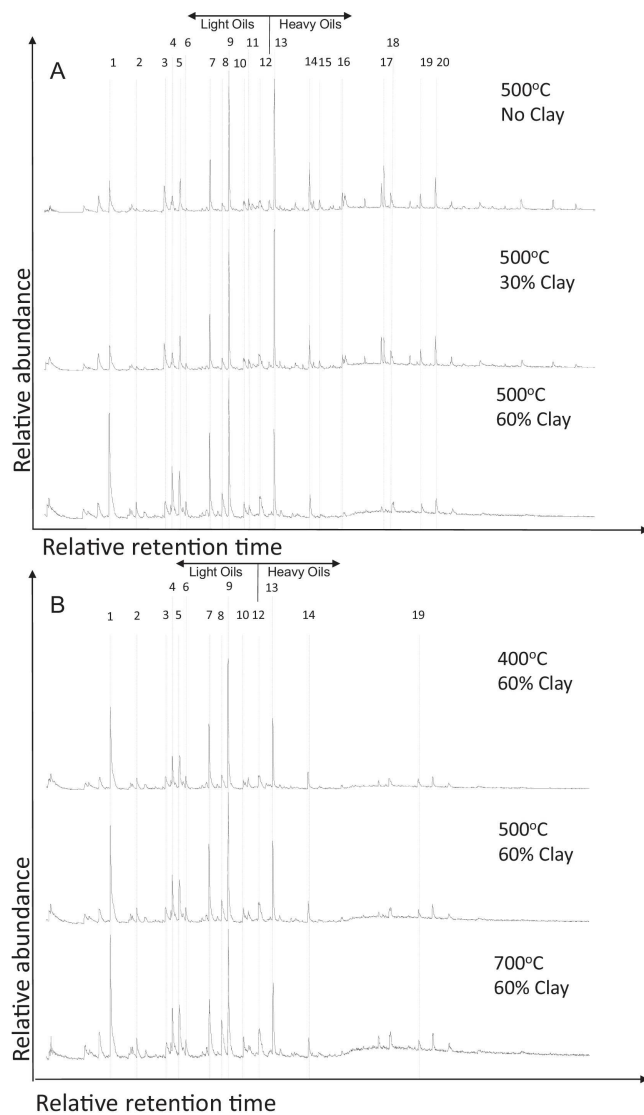
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412 Figure 6

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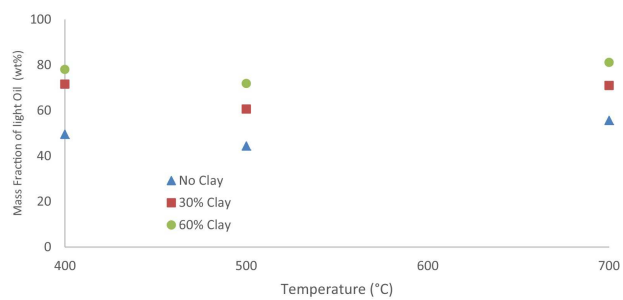


417 Figure 7

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