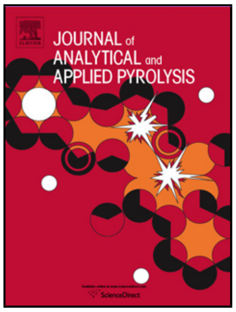

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Increased charcoal yield & production of lighter oils from the slow pyrolysis of biomass

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Highlights

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

Abstract

In an effort to reduce CO2 emissions from solid fuels, a considerable amount of research is going into how improve the manufacturing processes and product properties of the products from pyrolysis. One aspect that is often overlooked is the production of charcoal for cooking and soil remediation, which is an inefficient conversion process. There is considerable interest into using additives to increase charcoal yields, and based on the observation from fast pyrolysis work that certain catalyst tar cracking pathways can deposit considerable amounts of coke on the surface of the catalyst, there is a potential application to slow pyrolysis processes producing charcoal. Alumino-silicate catalysts have been shown to have a relatively high tendency to do this. This work hypothesises that this catalysation can be applied to slow pyrolysis, with low cost alumino-silicate minerals, specially bentonite clay, which has been added to pine pyrolysis in concentrations up to 60% wt (against input biomass) at temperatures 300 – 700°C.

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

Keywords

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

1 Introduction

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

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

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

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

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

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

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

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

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

The aim of this work is to see the effect that the addition clay mineral bentonite has on the extent of tar disproportionation into lower molecular weight oils, coke and gas as well as providing composition data on the oils obtained and showing how the composition simplifies with increasing clay concentration from slow pyrolysis of pinewood. This will be done over a temperature range from 400-700°C and clay mineral concentrations of up to 60%wt (compared to input biomass), a much greater range than presented in Veses, et al. [19]. Pinewood has been chosen for its abundance in European and American forests and its widely studied nature. It was hypothesised that the higher addition of clay mineral would produce higher charcoal yields due to the solid acid catalyst nature of the material; with the added benefit of better quality gas and lower molecular weight chemicals.

2 Materials and methods

2.1 Materials

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

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

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

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

2.2 Pyrolysis system

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

The HTF was pre-heated to 250°C to prevent effects on uncontrolled heating due to the furnace setup, then the biomass sample was introduced and heated to peak temperatures of 400, 500 and 700°C at a heating rate of 20°C/min. Dwell time at the peak temperature was 1 hour. The sand/clay/pinewood experiment was only carried out at 500°C only.

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

2.3 Charcoal characterisation

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

2.4 Liquid characterisation

Samples of the liquid were used for two analysis types:

- Gas Chromatography Mass Spectrometry (GC-MS) analysis for composition determination. 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 titrated until water collection volume was stable.

2.5 GC-MS analysis

Oil samples were weighed into a sample tube and diluted with dichloromethane. GC-MS in full scan mode (m/z 40-450) was performed on the samples with a Varian CP-3800 gas chromatograph, interfaced to a Varian 1200 mass spectrometer (EI mode, 70 eV). Separation was made using a ZB-1701 fused silica capillary column (60 m x 0.25 mm i.d., 0.25 mm thickness), with helium as the carrier gas, and an oven 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 up to number of carbon atoms (NC) 35.

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

3 Results and discussion

3.1 Changes in the system mass balance with clay addition

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

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

3.2 Changes in product streams quality

3.2.1 Effect of clay addition on charcoal quality

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

3.2.2 Effect of clay addition on oil composition

Figure 6A presents the GC-MS analysis of the liquid stream for 0, 30% and 60% clay concentration experiments at 500°C, to highlight the oil composition changes with clay concentration and Figure 6B shows the temperature effects from 500 – 700°C, at 60% clay concentration. Figure 7 breaks these streams down into heavy and light fractions, and shows that there is a significant cracking effect as light fraction increases from approximately 50% to around 80% of the total oils in the sample. From these plots, it can be seen there is considerable effect on the composition of the oil via the addition of clay. Figure 7 also indicates that there is some increase in the cracking effect by increasing temperature, as expected [9, 22] from previous studies but in terms of the relative cracking effect, increasing temperature only increases the total amount of oil cracked.

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

4 Conclusions

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

Acknowledgements

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List of captions

Figure 1. Setup of Gray King pyrolysis assay. Biomass and clay are loaded into the quartz retort tube and heated with the horizontal furnace.

Figure 2. Gas, solid and liquid phase yields of pine wood at 400°C (2A), 500°C (2B), 700°C with 6 concentrations of clay (0, 10, 20, 30, 40, and 60 (%wt). Gas yield is calculated by difference.

Figure 3 Changes in oil/pyrolytic water breakdown of liquid phase produced during pyrolysis at 400°C (3A), 500°C (3B) and 700°C (3C).

Figure 4. Change in product yields relative to no catalyst pyrolysis, dry ash free basis, at 400°C (3A), 500°C (3B) and 700°C (3C).

Figure 5. Volatile content of charcoal produced by pyrolysis, dry ash free basis.

Figure 6 Total ion chromatograms from the GC-MS of oils from pyrolysis: Plot 7A. Constant temperature, 500°C increasing clay concentration, 0 -60 wt% and Plot 7B. Constant clay concentration, 60 wt%, and increasing temperature 500 – 700°C. Arrows above the chart are indicating heavy and light oil fractions. Peak assignments: 1. furfural 2. 2 methyl cyclopent-1-one, 3. 1,2 cyclopentadiene, 4. 5 methyl furan carboxaldehyde, 5. 2-furanone, 6. 5 methyl furanone, 7. 2 hydroxy 3 methyl 2 cyclopent-1-one, 8. phenol, 9. 2 methoxy phenol, 10. 2 methyl phenol, 11. 3 methyl phenol, 12. 4 methyl phenol, 13. 2 methoxy 4 methyl phenol, 14. 4 ethyl 2 methoxy phenol, 15. Dianhydro glucopyranose, 16. eugenol, 17. 2 methoxy 4 propenyl phenol, 18. vanillin, 19. Hydroxy methoxy phenol 2 ethanone, 20. Hydroxy methoxy phenol 2 propanone.

Figure 7. Effect of clay concentration and temperature on fraction of light oils produced by pyrolysis. Distinction between heavy and light oil based on retention time above that of 4-methyl phenol; BP of 201°C, molecular weight, 108.13g/mol.

Figure 1

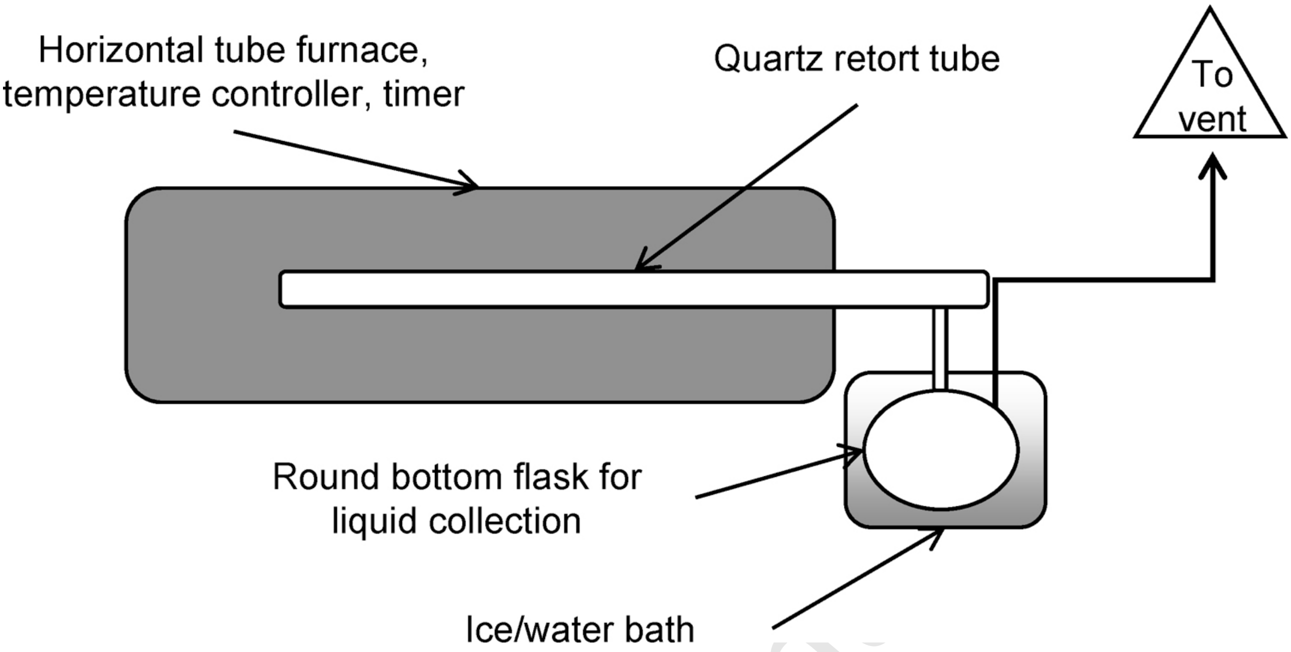

Horizontal tube furnace, temperature controller, timer
Quartz retort tube
To vent
Round bottom flask for liquid collection
Ice/water bath

Figure 2

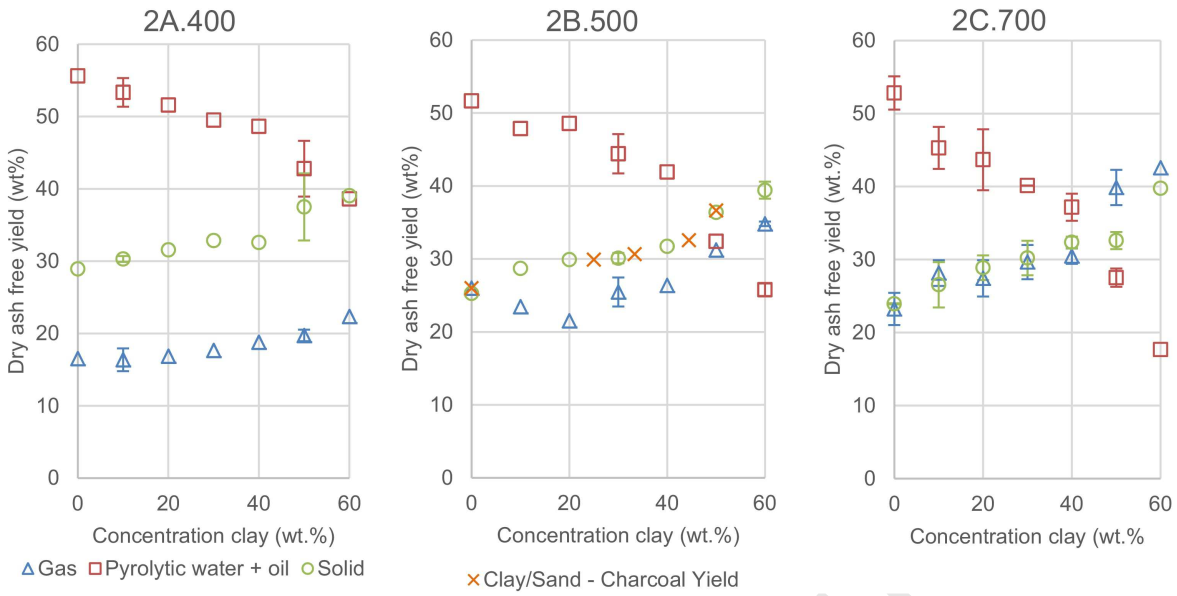
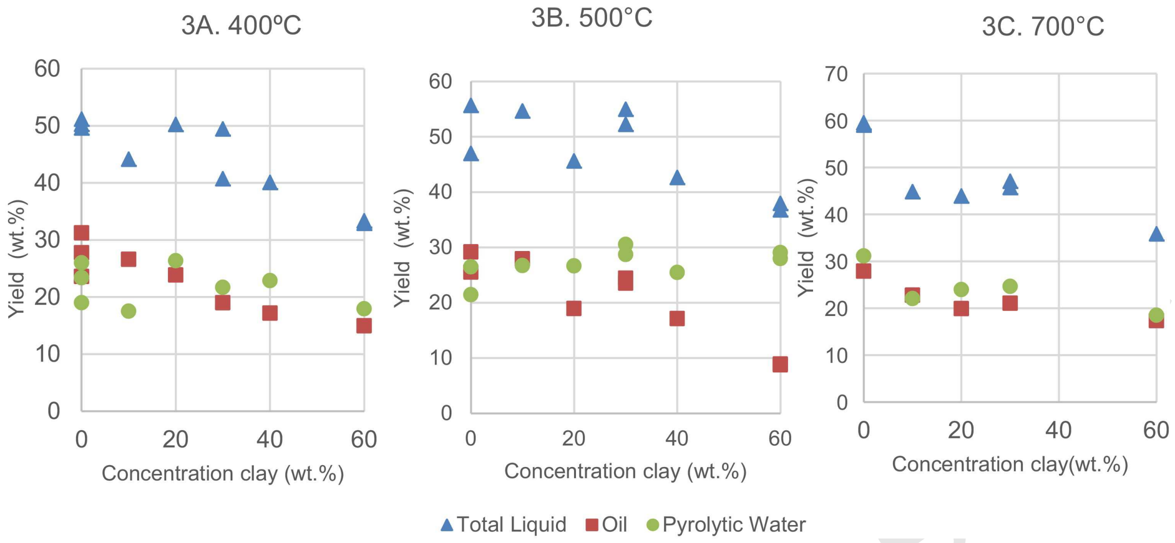
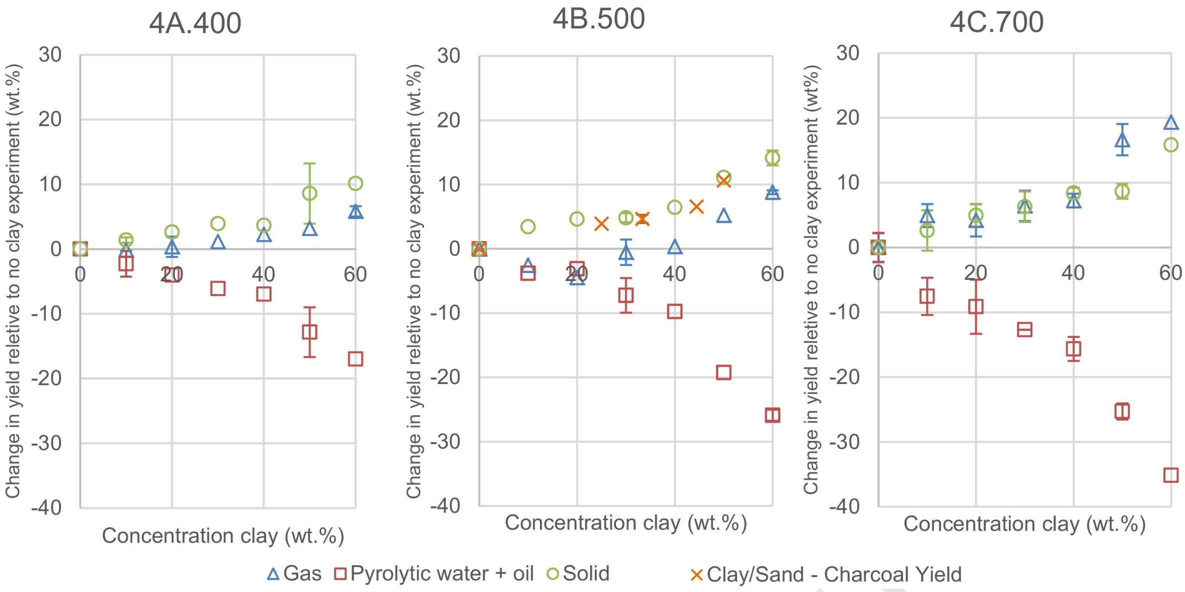

2A.400
2B.500
2C.700
Dry ash free yield (wt%)
Dry ash free yield (wt%)
Dry ash free yield (wt.%)
0
10
20
30
40
50
60
Concentration clay (wt.%)
Concentration clay (wt.%)
Concentration clay (wt.%
△ Gas
□ Pyrolytic water + oil
○ Solid
× Clay/Sand - Charcoal Yield

Figure 3


3A. 400ºC
3B. 500°C
3C. 700°C
Yield (wt.%)
Concentration clay (wt.%)
Concentration clay(wt.%)
0
10
20
30
40
50
60
70
▲Total Liquid
■Oil
●Pyrolytic Water

403 Figure 4

404



405

406

407

Figure 5

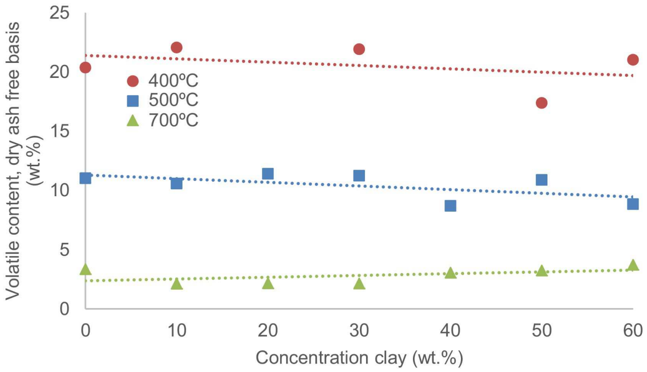

Volatile content, dry ash free basis (wt.%)
25
20
15
10
5
0
0
10
20
30
40
50
60
Concentration clay (wt.%)
400ºC
500ºC
700ºC

Figure 6

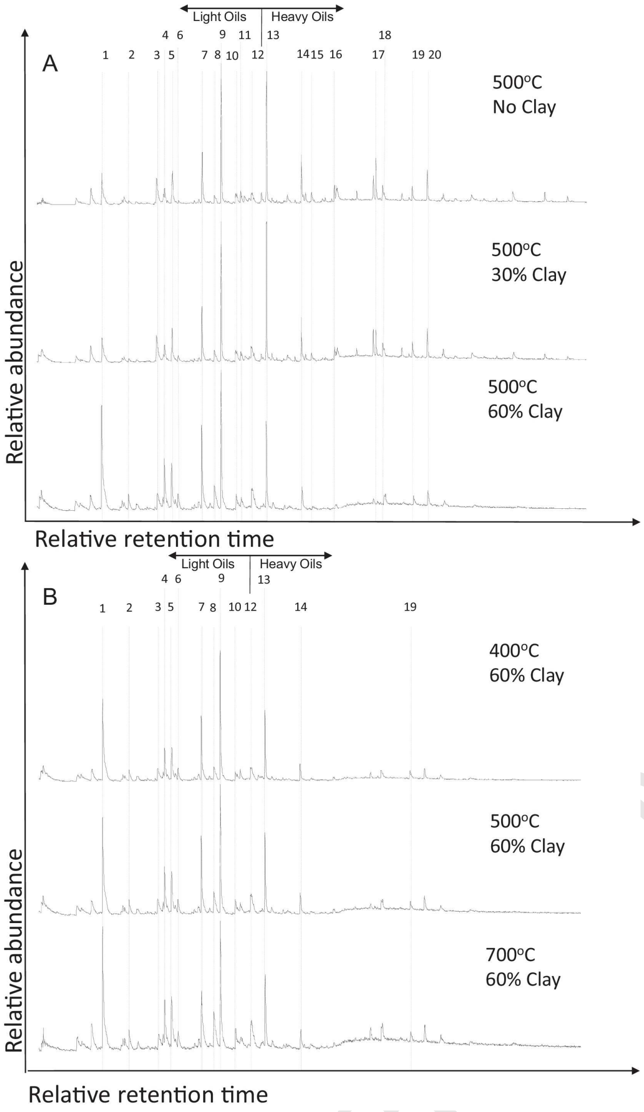
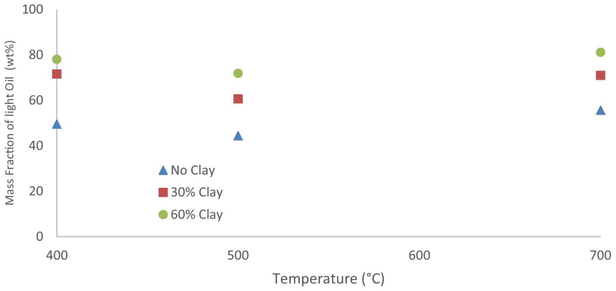

Light Oils
Heavy Oils
A
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
500ºC
No Clay
500ºC
30% Clay
500ºC
60% Clay
Relative abundance
Relative retention time
B
1 2 3 4 5 6 7 8 9 10 12 13 14 19
400ºC
60% Clay
500ºC
60% Clay
700ºC
60% Clay
Relative abundance
Relative retention time

Figure 7


100
80
60
40
20
0
Mass Fraction of light Oil (wt%)
400
500
600
700
Temperature (°C)
No Clay
30% Clay
60% Clay