University of Alberta

Hydrothermal Treatment of Low Rank Coal

by

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To my parents, brother and sisters for their support and love

Abstract

Abundance of low rank coal and increasing demand for energy provide an incentive for upgrading the low rank coal due to their high moisture and oxygen content. Various analyses were done to study the effect of the hydrothermal treatment on the physical and chemical structure of coal. Treatment of lignite coal results in a high reduction of moisture and oxygen especially at high temperature. Increasing the hydrophobicity and higher heating value of the coal are some advantages of hydrothermal treatment. Also increasing the initial pressure leads to decrease the energy required for the process and reduces the losing of volatile matter. In addition analysis of ash shows the reduction of alkali metals during the hydrothermal treatment. This should reduce slagging and fouling issues during coal combustion. This result is confirmed by analysis of extracted water.

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ASTM: American Society for Testing and Materials

BT: BaoTou Coal

C: Carbon

CWS: Coal Water Slurry

daf: dry, ash-free basis

db: dry basis

dmmf: dry, mineral matter-free

GCMS: Gas Chromatography – Mass Spectrometry

H: Hydrogen

HHV: Higher Heating Value

ICPMS: Inductively Coupled Plasma Mass Spectrometry

FTIR: Fourier Transform Infrared Radiation

LRC: Low Rank Coal

N: Nitrogen

O: Oxygen

POP: Poplar Coal

S: Sulphur

SEM: Scanning Electron Microscope

SF: Size Fraction

SHS: Superheated Steam

TOC: Total Organic Carbon

XM: XiMeng Coal

XRF: X-Ray Fluorescence

HTT: Hydrothermal Treatment

MTE: Mechanical Thermal Expression

1. Chapter 1: Introduction

Recently, high demand of energy and the concern of shortage of some sources of energy like oil and gas in near future make it essential to find other sources to address this huge need of energy. Coal is one of the main sources for providing a part of the required energy and especially for the electricity generation [1]. Coal can be divided into two categories, high rank coal and low rank coals based on their properties and different characteristics. Anthracite and bituminous coal is classified as high rank coal and low rank coal consists of sub-bituminous and lignite coal. As it comes from the name of the low rank coal the maturity and heating value of the low rank coal is lower in comparison with the high rank coal [2]. High moisture and oxygen content of the low rank coal [3, 4] are the main obstacles in using them and cause the environmental issues like green-house gas (GHG) emission [5]. High moisture and oxygen content lead to several disadvantages such as increasing the transportation cost, decreasing the efficiency of the plant, increasing the GHG emission, increasing the self-ignition tendency [5, 6, 7]. Therefore it is necessary to do the pre-treatment of low rank coal like removal of moisture or drying, removal of mineral matters and thus upgrading the low rank coal. Evaporation drying, microwave drying, mechanical thermal expression and hydrothermal treatment are some methods for drying and upgrading of the low rank coal [8]. Hydrothermal dewatering is a non-evaporative method which can remove the water from the coal as the liquid phase thus the latent heat of the water can be saved. In addition to that hydrothermal treatment can change the structure of the coal physically and chemically and upgrades the coal to a more value added one [4, 8]. During the hydrothermal treatment, water is being removed as liquid form under high pressure and temperature [4, 9]. During this process some organic components and alkali metals leach out from coal into the water and the coal tar or liquor generates an extra coating on the coal particles and prevents re-absorption of moisture [3, 8, 10]. At the same time some oxygen functional group such as carboxyl and hydroxyl group can break out and produce CO_2, H_2O and CO gases [9, 10]. Increasing the hydrothermal treatment temperature increases the amount of the CO_2 significantly, since the evolvement of the carbon dioxide is effective on removing the moisture from coal it can be one of the reasons for decreasing the moisture content at high temperature [11]. Due to reduction of oxygen functional groups and coating the surface of coal the hydrophobicity of coal increases [3, 4].

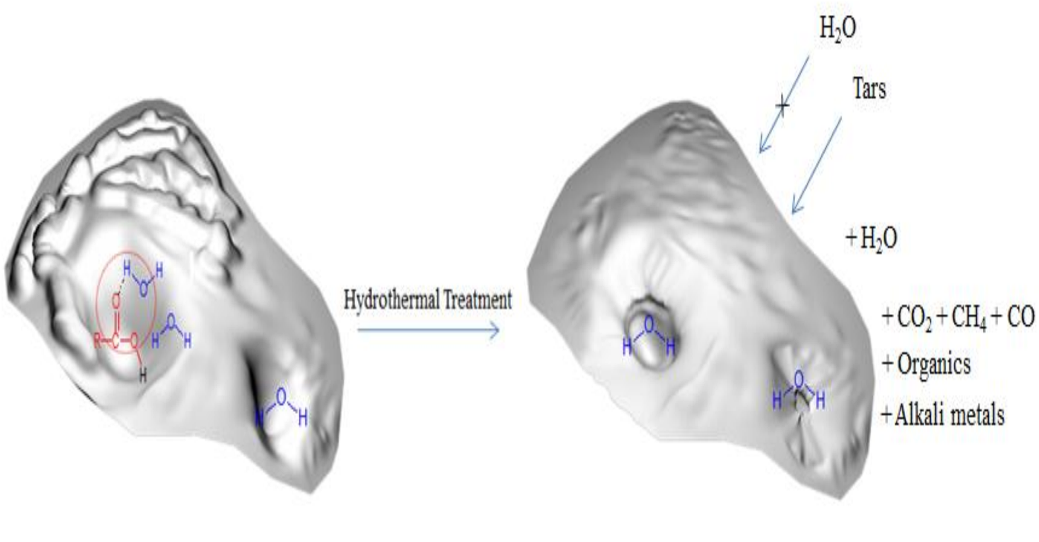

Figure 1.1: Schematic representation of hydrothermal treatment (Top view)

Figure 1.2: Schematic representation of hydrothermal treatment (Side view)

The aim of this study is to investigate the feasibility of the hydrothermal treatment on:

- Dewatering or removal of moisture and upgrading of the coal to a higher value added one and to investigate the mechanism for hydrothermal treatment process.
- The effects of the size fraction of the coal particles on the removal of moisture
- The effect of residence time on the removal of moisture and coal elements
- The effect of the initial pressure of the batch reactor on the removal of moisture and the efficiency of the hydrothermal treatment process.

2. Chapter 2: Literature Review

2.1. Formation of Coal

Coal is one of the main sources for producing energy, especially with the concern of shortage of energy for the future, the industry has become keen about the coal. The basis of formation of the coal is plant debris that was decomposed “to simpler compounds and buried under silts by land subsidence and changing of local water regime” [12]. The silts cover the plant residue and prevent more decay, in addition to that high pressure of sediment compact plant residue and heat changes it chemically, under appropriate conditions the formation of peat is initiated. Formation of peat is the initial step for formation of the coal. Finding coal in different area shows this fact that formation of coal is not dependent on a special type of plant debris [12, 13].

2.2. Digenesis and Metamorphism

Significant difference in the processes of plant debris before and after burial causes the coal formation was classified into two stages. Extensive biochemical reactions is main parameter in first stage that is called digenetic stage and abiotic thermal changing of organic mass is the main parameter in the second stage that is called metamorphic stage [12]. Metamorphic stage may cause changing the minerals but the main effect of metamorphic stage is on the organic materials which can change the value of the coal and divide it to several types [14].

2.3. Characterisation of Coal

Usually coals are characterized based on chemical composition and physical and mechanical properties. The changes during the transformation of the peat to the coal are called coalification. It is important to know how the properties and chemical composition of coal change. Geological maturity (rank) is the main factor in determining the properties and chemical compositions of the coal, the properties of each coal can discern different types of coal. Rank is a qualitative definition that shows the maturity of coal during its metamorphic change. As indicated in part 1.2 during the metamorphic stage, the main components for altering are organic materials, thus organic rich fraction has to be analyzed to determine the rank of coal [13,14].

Classification of coal is strictly depends on its application, there are two main systems for classification of coal: "commercial and scientific. In commercial classification, trade and market, behaviour of coal, utilisation properties are the main aspects of coal but in scientific classification, origin of coal, constitution are the main aspects of coal" [14].

2.4. Coal Analysis

For determining the chemical composition of coal two kinds of analysis are executed on coal [14]:

1. Proximate analysis

   The relative amount of moisture, ash, volatile matter and fixed carbon are measured by this analysis.

2. Ultimate analysis

    The amount of chemical elements such as carbon, nitrogen, hydrogen, sulfur and oxygen are determined in this analysis.

2.5. Low Rank Coal

It is estimated that nearly half of the coal reservoirs of the world are low rank coal (LRC), such as lignite and sub-bituminous coal [3, 6]. 60 % of Greece electric energy is produced by using lignite coal [15] and lignite plays an important role in electricity production in Victoria, Australia [16]. The metamorphic change during the coal formation is not complete for LRCs and they have lower heating value in comparison with higher rank coals, i.e., anthracite and bituminous coal [2]. LRCs are younger than higher rank coal and usually can be found in seams with less overburden thus LRCs have low mining cost that makes them noticeable as source of energy.

2.5.1. Moisture

The amount of moisture in low rank coal is very high, typically 25 - 66 wt %, which depends on the different mining regions [3]. For example Victorian brown coal consists of 66 wt % [17] moisture whereas the moisture amount in Silesian anthracite is just 0.6 wt % [18]**.** This high amount of moisture leads to several major problems during the using the low rank coal and is the main reason for not utilizing the LRCs widely. Efficiency of the plant and net energy of output decreases due to the evaporation of water in the low rank coal. Combustion of wet coal requires almost 7 - 10 % [6] of input fuel to evaporate the moisture and produces larger volume of flue gas that needed larger boiler for the plant.

Transportation of LRC is also not economical due to high percentage of moisture content [6, 7]. Thus removing moisture from low rank coal is one of the main operations before utilizing them.

Knowing different types of moisture which exist in coal helps to design an appropriate and ecumenical method for removing moisture.

It is reported [6] there are different types of moisture in coal:

1. During the formation of coal some amount of water set down in micro-pores and micro-capillaries.
2. A layer of water exists near to the coal molecules only on the surface of the coal particles.
3. There are some narrow cracks within the coal particles, some amount of water exists in this narrow crack which called capillary water.
4. Usually between the coal particles there are some spaces which water can exists there.
5. Adhesion water which exists around the individual or more coal particles.

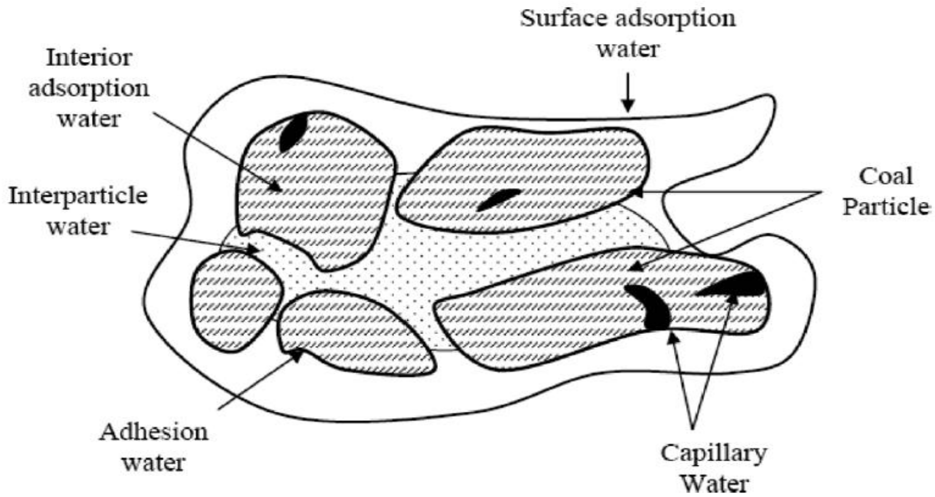

Figure 2.1: Different types of water [6]

These types of moisture can be classified as surface and inherent moisture. Adhesion water and Inter-particle water can be classified as surface moisture and can be removed from coal by mechanical or thermal process. Interior adsorption water, surface adsorption water and capillary water can be classified as inherent moisture and can be removed by chemical and thermal process.

2.5.2. Other characteristics of LRC

High weathering ability, high amount of generation of dust and low friability are some characteristics of low rank coal [7, 19]. LRC also have higher volatile matter and less fixed carbon in comparison with higher rank coals [2]. Table 2.1 summarizes the proximate analysis of some LRCs from different regions:

Table 2. 1: Proximate analysis, wt % (As Received) [2, 17]

LRCs	Moisture	Volatile Matter	Fixed Carbon	Ash
Fort Union Region Lignite	37.2	26.3	30.3	6.2
Gulf Region Lignite	30.8	30.8	24.9	13.5
Powder River Subbituminous	25.4	29.6	38.7	6.3
San Juan Basin Subbituminous	12.8	33.1	40.6	13.5
Loy Yang Brown coal	62.5	19.24	17.7	0.56

In addition of high moisture content, the LRCs consist of hydrocarbons containing oxygen functional groups such as hydroxyl (-OH) and carboxylic acid (-COOH) groups. These characteristics of LRCs are the one of the main obstacles in using them widely [8, 9]. Because of hydrophilic behaviour of low rank coals the floatability is poor [20]. Self- ignition tendency is another problem that has to be considered during the transportation and storage of LRCs. High self-ignition tendency is mainly due to high content of oxygen in LRCs. In addition decreasing the plant efficiency, increasing the maintenance cost, and making the grinding process more difficult while using the LRCs are some reasons that convince us to treat the coal before combustion or gasifying [6, 21, 22].

Even though low rank coal is not as qualified as high rank coal, they have some advantages over high rank coal. LRCs are younger than that of higher rank coal and usually can be found in seams with less overburden [3]. Reactivity of low rank coal is high and their high amount of volatile matter is favorable for combustion [19]. Pollution impurities amount such as nitrogen, sulphur and heavy metals is low in the low rank coal which makes the industry more eager to use the low rank coal [3].

By considering the advantages and disadvantages of low rank coal, dewatering and upgrading of the low rank coal is an essential part to remove the negative effects of low rank coal. “Recent work at Monash University, Australia shows that by 30 % of green-house gas emission can be reduced by moisture reduction in Australian lignite” [6]. According to Lucarelli [23] just by drying the coal from 35 to 25 wt% moisture content of coal, $ 0.19/GJ of energy can be saved on storage, transportation and handling of LRCs. Coal is used for several purposes such as coking, gasification, briquetting and ..., each purpose requires different final amount of moisture. Brown coal with high moisture content is not suitable for gasification or liquefaction [24]. Table 2.2 shows the approximate range of moisture for different process. For applying the low rank coal for these processes, they have to be dried before application due to high amount of moisture.

Table 2. 2: Approximate range of moisture for different process [6]

Type of coal	Usage of coal	Optimum moisture content (wt %)
Hard Coal		
	Coking processes (based on the ramming method)	8 – 12
	Coking process (based on the charring method)	< 8
	Briquetting process	< 4
	Low-temperature, carbonization process	~ 0
	Hydrogenation process	~ 0
	Coal combustion process in the pulverized fuel fired furnace	< 2
Brown Coal		
	Briquetting process	8 – 18
	Gasification process	5 – 15
	Low-temperature, carbonization process	< 15
	Hydrogenation process	~ 0
	Coal combustion process in the pulverized fuel fired furnace	12 – 15

Several methods for dewatering and upgrading of the coal have been used so far such as evaporative drying, microwave drying, mechanical thermal expression and hydrothermal treatment [8]

2.6. Drying, Dewatering and Upgrading

There are different methods for dewatering and upgrading of the coal. In each method we have to consider some points to avoid the negative consequences.

Coal changes physically and chemically during the drying process [25]. Spontaneous combustion is one the problems after drying if the appropriate actions have not been taken. Usually for avoiding the spontaneous combustion, the drying process has to be done by low oxygen content medium. One way is using the superheated steam method. Using this method needs high capital cost due to generating steam and running the system [19]. Steam drying method can be applied to higher moisture content fuel [26]. Another way is using the hydrothermal treatment, in this method by changing the structure of the coal and removing some oxygen functional group [9], the spontaneous combustion ability decreases. By utilizing the indirect system for drying the coal, spontaneous combustion can be prevented. In this method the low rank coal and medium which is oxygen-rich have the minimum direct contact [6].

Explosion of LRCs when the dried low rank coals are exposed to high moisture environment is another problem dealing with low rank coal especially when the smaller size fraction of coal is used for drying [27] thus appropriate storage of dried coal is needed to prevent self-ignition and minimizing the re-absorption of moisture. Loss of volatile matter during the drying specially at high temperature is another problem. Loss of volatile matter decreases the higher heating value of the coal. By using low temperature for drying or by providing a vacuum environment, the loss of volatile matter can be lowered but these methods for reducing the volatile's loss decrease the drying rate [19]. Drying cost is a main parameter for all kinds of drying. Many drying methods and systems exist for dewatering of the coal but all of them are not appropriate for low rank coal. There is a wide difference in characteristics of low rank coal in different regions, hence the dryer has to be selected based on the bulk properties of low rank coal. Table 2.3 shows the different properties of low rank coal in different regions.

Table 2. 3: Properties of low rank coal in different regions [19]

Region	Calorific Value (MJ/Kg)	Moisture (wt %)	Fixed Carbon (wt %)	Volatile Matter (wt %)	Sulfur, daf (wt %)	Ash, db (wt %)
Australia	5 to 14	44 to 71	65 to 70	25 to 30	0.1 to 5	0.5 to 13
Bulgaria	5 to 14	14 to 62			3 to 11	28 to 58
China		14		46		8
Czech Republic	9 to 19	6 to 55			0.7 to 9	7 to 44
Germany	7 to 12	12 to 51	17 to 20	52 to 62	0.4 to 4	5 to 11
Hungary	6 to 15	19 to 48			0.8 to 5	18 to 40
Indonesia	21 to 23	15 to 22	37 to 40	37 to 41	0.5 to 4	2 to 8
Poland	7 to 22	9 to 55			0.5 to 7	8 to 40
Spain	12 to 17	13 to 24			3 to 12	17 to 70
Turkey	20 to 28	6 to 20	29 to 46	45 to 56	1.8 to 14	3 to 20
USA						
Montana	24 to 25	37	31	25	0.48	7
North Dakota	16	34 to 44	25 to 33	24 to 30	0.2 to 1.4	4 to 8
Texas	15	32	26	28	0.7	14
Wyoming	17 to 22	21 to 37	30 to 41	27 to 36	0.2 to 1.2	4 to 12

2.6.1. Thermal drying

In evaporation drying method, air or combustion gas is used for removing moisture from coal. In this method water in removed from coal as water vapour, CO and CO_2 which the amount of these two compounds is considerably less that water vapour. Depends on the characteristics of coal, direct or indirect drying may be used for dewatering of the coal. One of the main problems of evaporation drying is high energy which has to be consumed for removing the moisture, in some cases requiring 20 % chemical bounded energy of coal. This results higher emissions of CO_2 per unit of dried coal [6, 8, 17]. In evaporation method like other methods safety consideration due to high potential of explosion is in priority. Hot medium with the temperature as high as 700 – 900 °C at the inlet of dryer and 60 – 120 °C at the outlet can be used. At this high temperature by considering the high reactivity of low rank coal it is important that the medium has low amount of oxygen content to avoid explosion hazards [6]. Usually the dried coal by evaporation method is used online due to possible explosion during the storage and transportation.

During the evaporation method, the bulk moisture diffuses to the surface through the pore structures and evaporates from the surface of coal. In the drying process, first, the coal sample absorbs the heat and temperature of it increases in a short period of time (initial transient). Then, slow drying from the surface of the coal follows the constant rate, when the rate of drying is more than diffusion of the bulk moisture, the rate of drying starts to decrease and the surface get dried and evaporation occurs in the coal particles [7, 17, 28, 29]. Significant shrinkage occurs during the evaporation drying which cause substantial stress in large particle [17]. Figure 2.2 shows the drying rate of coal for different temperatures:

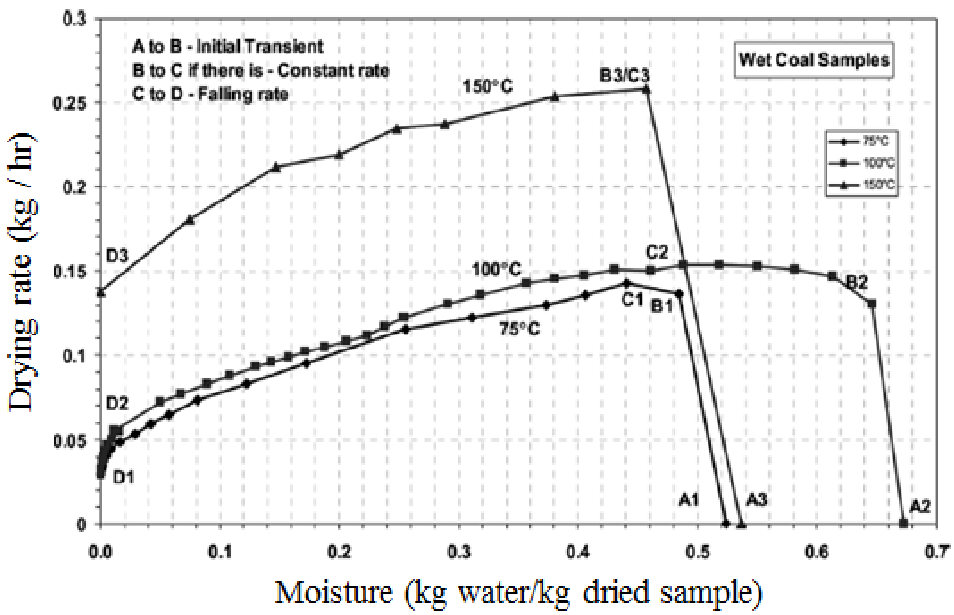

Figure 2.2: Drying rate of wet coal at different temperatures [7]

Several instruments for direct and indirect evaporative drying have been designed. Each one has its own advantages and disadvantages.

Fluidized bed dryer is used in various industries and reported [30, 31] to have high rate of drying because of well mixing of drying medium and wet solid but high pressure drop is disadvantage of this kind of dryer. “Another problem is scaling up due to the complex behaviour of bubbles and mixing regimes in different size of dryers” [32]. Park et al. [33] reported that about 80 - 90 wt % of moisture in Indonesian coal can be reduced by fluidized bed dryer. Vibrated bed dryer was reported [34] to provide the low velocity which is needed for fluidization. Pneumatic dryer [30] is reported not to have complex construction but attrition is the problem here. Rotary dryer [6, 30] is reported that has high efficiency in comparison with other kind of dryers, using a medium with low oxygen content is other benefits of rotary drying which decreases the possibility of explosion, although the maintenance cost of this dryer in high. Table 2.4 summarizes the properties of some dryers.

Table 2. 4: Properties of some dryers [6]

Dryers	Characteristics of drying method
Rotary	Coal or coal muds. Concurrent mode to avoid ignition, hot air, or combustion gases, heat consumption (3700 kJ = kg H_2O), drying time (14 to 40 min)
Rotary-tube	Widely used in brown coal briquetting plants, also for hard coals. Indirect dryers heated by saturated steam (0.15 – 0.55 Mpa)
Chamber	Commonly used for flotation concentrates, dryer equipped with stirrers, concurrent mode, hot combustion gases, can break sintered coal
Pneumatic	Coal or flotation concentrates, conditioned by the heating medium velocity and the grain size of coal. Short drying time
Fluid bed	Intense drying due to good mixing, high-temperature heating medium, high porosity in the dryer
Spouted fluid bed Vibratory	Fine-grained coal or coal mud, combustion gas or air with low temperature (< 200 °C) Hard and brown coals, combine coal transport, proportioning and drying operations, hot air or combustion gases, also used for cooling coal
Mill type	Combing grinding and drying operations, generally used in power plants using steam boilers fired by pulverized coal

2.6.2. Microwave drying

Low rank coals consist of high moisture content in their structure thus there are many dipoles molecules in low rank coal. This criterion leads to introduce new drying method calling microwave drying. The materials which have high free water generally absorb the microwave by dipole rotation mechanism [35]. When low rank coal is exposed to the microwave field, ion and polar functional group start to move due to electric field. They align their-self with electric field, by using alternative electric field the orientation of these compound changes many times in one second, this movement and changing in the orientation cause the friction between the molecules so the electric energy finally is converted to the heat which can remove the water from low rank coal [35]. The process of drying in evaporation method is slow because in this method, the surface is heated and the transfer of heat to the core depends on the properties of coal and particle size but in the microwave drying the energy is directly transferred to the water, this cause better efficiency and decreases the time for drying [19]. Another advantage of microwave drying is the selective heating. If different dielectric properties exist in the material, the component which has high dielectric loss factor is the main target of microwaves, in wet material water has this criterion which results in absorbing the microwaves [35]. The effect of the microwave radiation on the calorific value is the same as conventional drying [36]. High capital and maintenance cost in microwave drying is one of the problems for applying this method commercially [19], uneven drying and changing in the dielectric properties of material are other problems of this method [35]. Over drying in microwave method always is a concern regarding to the safety of operation during the process [37, 38].

2.6.3. Mechanical thermal expression

By combination of press dewatering and heating the coal samples the moisture in low rank coal can considerably decrease. It is reported [39] about 55 - 75 wt % of inherent moisture can be removed by applying mechanical thermal expression at 12 Mpa and 150 °C.

Study on Mechanical dewatering of high moisture content lignite [40, 41] shows that this method can remove the moisture from coal. In comparison with evaporative drying removing water mechanically can reduce the required energy [42]. Banks et al. [41] reported this method can decrease the moisture content of coal significantly. For removing moisture by mechanical press, high pressure has to be applied to the system for a long residence time, this causes lower intention toward this kind of dying. Hell et al. [41] reported applying a 54 Mpa pressure results 21 wt % moisture reduction in the Loy Yang lignite. Guo et al. [43] applied the mechanical expression on the hydro-treated brown coal to further destruction of coal porosity and increasing the solid concentration in the slurry.

Improving the mechanical press resulted in mechanical thermal expression which started by Strauss and co-works at the university of Dortmund, Germany [17].

Using the mechanical thermal expression causes to apply lower mechanical pressure (e.g. 2 - 12 MPa) [17] in comparison with mechanical expression and the temperature that has to be applied for this method is relatively lower than hydrothermal treatment which reduce the contamination of the wastewater and reduces the loss of volatile matter through the drying process. Micro-porosity and moisture content of coal can significantly decrease by mechanical thermal expression [41, 42]. In this method the pores in the coal collapse during the process, and this irreversible collapse decreases the tendency of coal for reabsorbing of the moisture after dewatering [41]. Efficiency of MTE process in moisture removal increases by decreasing the rank of the coal [44].

According the calculation of Bargains and co-workers [17], by reduction of the moisture content of brown coal from 65.5 wt % to final moisture content of 25 wt %, the power generation efficiency can increase between 13 and 21 %.

2.6.4. Hydrothermal treatment

Among these methods of drying, hydrothermal treatment is a well known, non-evaporative method that upgrades the coal to a value added one by chemically and physically changing the structure of coal.

Fleissner developed the concept of hydrothermal dewatering in the 1920's in Austria. In this process the coarse lump of low rank coal is treated with steam at the temperature range of 180 - 240 °C in a batch autoclave reactor [17].

The Fleissner process was piloted in some area such as Victoria and some part of Europe [41, 45]. Kami et al. [17] improved the heat recovery of the process and this Japanese version was piloted in the 1980's. The Fleissner process with a commercial scale was built in the former Yugoslavia [19, 41].

Evans et al. [46] could make some changes in the process and improve the heat transfer. In their method steam is not used for drying of low rank coal, instead of that the coal is heated as slurry of water and coal [46]. It is reported that about 75 wt % of moisture consists in the lignite coal can be removed from its structure as liquid form at the temperature higher than 250 °C [41]. Favas et al. [47] reported that HTT is more beneficial for lower rank coal in comparison with high rank coal in many aspects such as afm calorific value and volatile matter.

In hydrothermal treatment coal is mixed with water and is treated under high pressure and high temperature. If the initial pressure is zero, during the process the pressure of system is equivalent to the saturated steam pressure. Operation at high pressure causes avoiding the evaporation of moisture in coal hence during the hydrothermal treatment the moisture in coal is removed as liquid form thus makes this process economically feasible and save more energy. This process can be used for lump, granular or for slurry of coal [17]. Yu et al. [4] conducted the hydrothermal treatment on a Chinese coal (XiMeng) by initial moisture content of the 18.38 wt %, and showed significant amount of moisture can be removed during the hydrothermal treatment. Figure 2.3 shows the effect of hydrothermal treatment on the moisture content of the coal.

Murray et al. [11] reported “the removal of liquid water is initiated principally by a disruption of the coal/water interactions caused by the thermal destruction of functional groups. The process is then completed by expulsion of water by the carbon dioxide evolved” [11], Shrinkage of the coal structure during the hydrothermal treatment and changing the hydrophobicity of coal by losing the hydrophilic groups cause the reduction and expulsion of the moisture from the coal structure.

More functional groups break down to H_2O, CO and CO_2 by increasing the treatment temperature, resulting more moisture can be removed from the coal by evolution of the CO_2 which increases the hydrophobicity of the coal [9, 11].

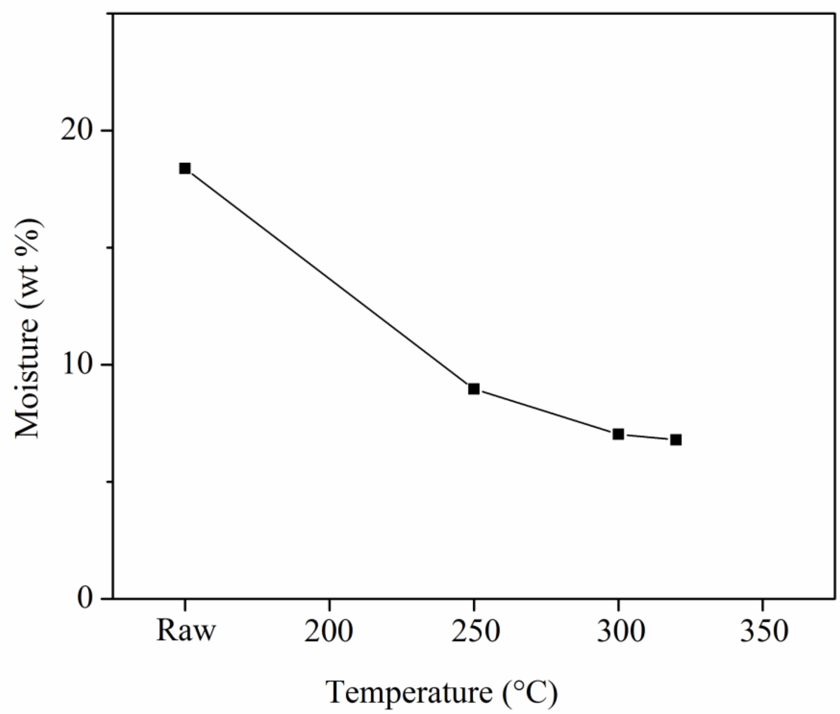

Figure 2.3: Effect of hydrothermal treatment on the moisture content of the coal [4]

Usui et al. [48] conducted vacuum drying and tar coating process at 300 °C on the Indonesian low rank coal and could decrease the moisture content from 19.9 to 5 wt %.

Allardice et al. [17] reported that during the hydrothermal treatment some soluble inorganic matters are dissolving in water and can be removed from coal. Presence of these mineral matters in the coal causes slugging and fouling issues during coal combustion and damages the boilers of the plant. During the hydrothermal treatment some of these mineral matters dissolve in water liquor and reduce the mineral matters amount in the treated coals [17].

One of the problems of coal drying at high temperatures is loss of volatile matter during the process which is not favorable for combustion due to reduction of heating energy. Hydrothermal treatment like other kinds of drying has some effects on the volatile matter content, especially at high temperatures that the loss of volatile is considerable. Zhao et al. [9] performed the hydrothermal treatment on the slurry of Canadian lignite coal and water with a coal to water ratio of 1 : 3 at different temperatures and showed volatile matter content can decrease by 23.4 wt % when the low rank coal is treated at 300 °C for 30 minutes.

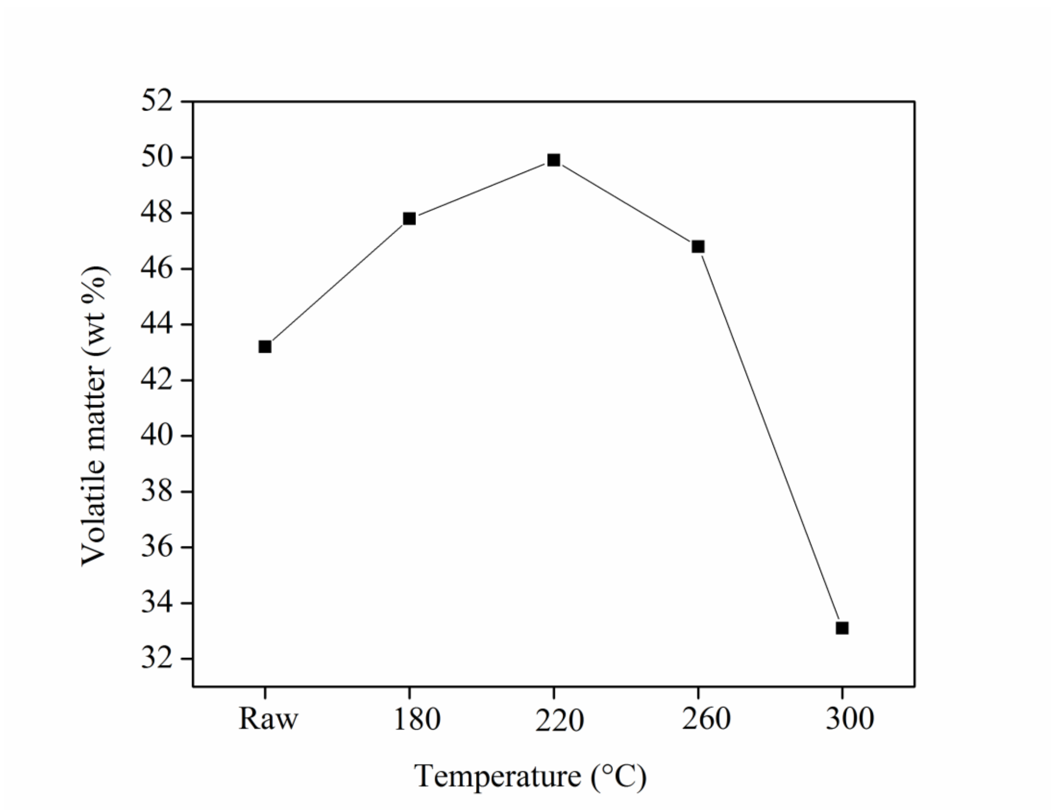

Figure 2.4: Effect of hydrothermal treatment on volatile matter [9]

As seen in the figure 2.4 by increasing the temperature of hydrothermal treatment initially, there is an increase in the volatile matter percentage which is due to reduction in moisture percentage. At high temperature the loss of volatile matter is high which is the disadvantage of hydrothermal treatment. We have to consider that a part of volatile matter which is removed from the coal migrates to the water which has to be recovered to prevent the organic contamination of wastewater [17]. Ross et al. [49] reported the presence of the phenols and dihydroxybenzenes in the recovered water of hydrothermal treatment at 350 °C on Wyodak coal. Favas et al. [10] conducted hydrothermal treatment on Loy Yang Low Ash mixed with water with coal to water ratio of 1 : 3 and found that the amount of total organic carbon increases in water by increasing the hydrothermal temperature and also the time of treatment can change the TOC in water. Increasing the residence time, increases the TOC in wastewater although not as much as temperature. Table 2.5 shows the effect of hydrothermal treatment on TOC extracted to wastewater:

Table 2. 5: Effect of hydrothermal treatment on TOC [10]

	250 °C	**280 °C**	**320 °C**	**350 °C**
10 (min)	0.3 (g/l)	0.8 (g/l)	2.6 (g/l)	5.4 (g/l)
30 (min)	0.4 (g/l)	2.1 (g/l)	4.2 (g/l)	6.7 (g/l)
60 (min)	0.8 (g/l)	3.0 (g/l)	4.6 (g/l)	6.9 (g/l)

During the hydrothermal treatment in addition of removing the moisture, low rank coal changes physically and chemically, this process leads to change the low rank coal to more value added one and increases the heating energy of LRCs.

Hydrothermally treated coal can decrease the reabsorption ability of low rank coal by changing the structure of the coal. During this process the pore structure of coal collapses and tar can coat the surface of the coal particle, in addition decarboxylation during the hydrothermal treatment can decrease the hydrophilic group thus decreases the re-absorption ability of low rank coal. At higher temperatures decarboxylation occurs more intensely [41, 50], hence it is expected that coal treated at higher temperature absorbs less moisture afterwards. Carboxyl and hydroxyl groups can break out during the hydrothermal treatment and produce CO_2, CO and CH_4. This reduction in carboxyl and hydroxyl group decreases the amount of oxygen functional groups which are hydrophilic, by reduction of hydrophilic group, the tendency of coal for absorbing the moisture decreases and hydrophobicity of coal increases. Laursen et al. [51] did the FTIR analysis on the raw (as received) and hydro-treated (300 °C for 30 min) Loy Yang coal and observed that carboxyl group peak decreased significantly by hydrothermal treatment, also the OH- group peak reduced considerably.

Zhicai et al. [52] performed the hydrothermal treatment on slurry of Chinese subbituminous coal and water. 10 g of Chinese coal was mixed with 20 g of water and the slurry was treated for 1 hour at different temperatures, it was reported that at 350 °C the emission of CO_2, CO and CH_4 was 10 (mg/g), 0.29 (mg/g) and 1.69 (mg/g) respectively.

Migration of waxes to surface of coal at high temperature during the hydrothermal treatment can increase the hydrophobicity of low rank coal [41, 53]. Yu et al. [4] analyzed the hydrophobicity of coal by measuring the contact angle.

Two Chinese coal (XiMeng (XM) and BaoTou (BT)) were mixed with distilled water with a coal to water ratio of 2 : 3 and treated hydrothermally for 1 hour. The results show significant increase in contact angle especially at 300 °C and 350 °C.

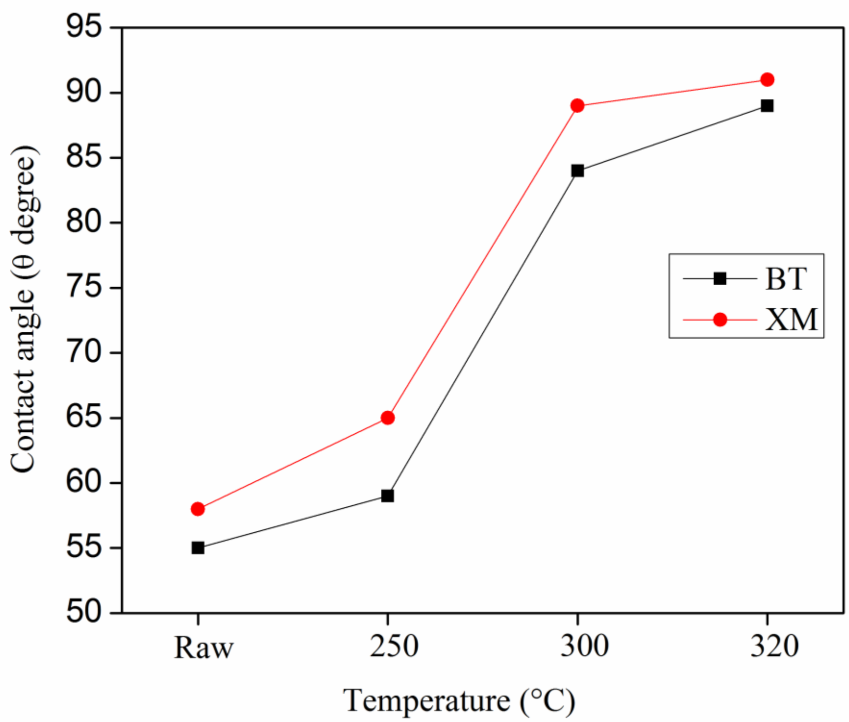

Figure 2.5: Effect of hydrothermal treatment on contact angle [4]

Hydrophobic coal has better slurry ability in comparison with hydrophilic coal. The water holding in the lignite coal due to large number of oxygen functional group is high, therefore the ratio of free water in slurry made by lignite coal is low and viscosity is high. Water repulsive surface of coal after hydrothermal treatment improves the slurry ability of coal [4]. Yu et al. [4] reported the maximum solid concentration could increase from 45.7 to 59.3 % by doing the hydrothermal treatment on a Chinese coal.

Potas et al. [54] reported that hydrothermal treatment of low rank coal can decrease the inherent moisture content to one third and make the coal more hydrophobic after the treatment and save 94 % of the energy remaining in the product.

Hashimoto et al. [17] reported in their process for upgrading the low rank coal they could reach to high solid density slurry (> 60 % db) by adding the chemical to the slurry of coal and water. However using a different method for measuring the viscosity may be the reason for this high solid density slurry.

Favas et al. [55] conducted a combination of evaporative drying and hydrothermal treatment on a brown coal and could achieve product with low porosity which can produce slurry with better pump ability.

Hydrothermal treatment has some effects on the floatation ability of low rank coal. Zhao et al. [9] conducted the hydrothermal treatment on a sample of Canadian lignite coal at different temperature for 30 minutes and observed that for certain floatation time the cumulative recovery increases by increasing the temperature of hydrothermal treatment. Figure 2.6 shows the floatation performance of raw and hydro-treated coal at different temperatures.

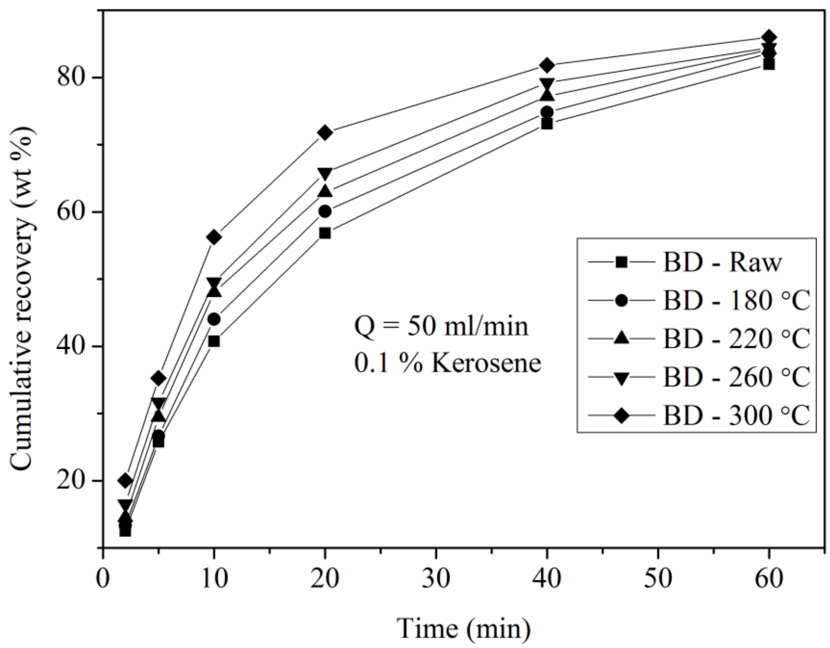

Figure 2.6: Effect of hydrothermal treatment on Flotation ability of low rank coal [9]

Sometimes the hydrothermal treatment can be done without adding extra water. In these cases the low rank coal has high amount of moisture content, the hydrothermal treatment can be done just by using the moisture in the coal. Treatment under high pressure in hydrothermal process prevents the evaporation of the moisture in the coal and the water can be removed from the coal as liquid phase. If the low rank coal consists high moisture content, this high amount of the moisture content can produce the required pressure thus the hydrothermal condition can be provided. Sakaguchi et al. [8] conduct the dewatering process on Loy Yang coal with initial moisture amount of 59.4 (wt %, as received) without adding extra water at different temperatures for 30 minutes. By measuring the temperature and pressure during the treatment they observed that the hydrothermal conditions were realized during the process. Operating the hydrothermal treatment without adding extra water has several advantages such as low final moisture content, reduction of oxygen content, less waste water and significant increase in the gross caloric value [8].

High capital cost of hydrothermal treatment instrument especially heat exchangers and cleaning the wastewater are the main concerns although this method has high potential in upgrading the coal and make it to more safe and environment friendly fuel and will be more attractive by decreasing the high rank coal sources [17].

3. Chapter 3: Experiment Setup

3.1. Coal Preparation

All hydrothermal experiments described here were conducted on a Canadian lignite coal (Poplar). For reducing the particle size and homogenizing the coal, it was grinded using a ball mill and blended before hydrothermal treatment. The ground coal was sieved for choosing different size fraction ranges. The size fraction less that 500 µm and between 500 µm to 1 mm were chosen for the hydrothermal treatment. The coal sample was stored in sealed plastic bag by releasing most of the air and was kept in refrigerator for avoiding oxidation and absorbing moisture. The raw coal (as received) initially has a high amount of moisture content 26.85 (wt %). Other components of lignite coal were (wt % db) ash 40.5 %, volatile matter 34.65 %, and fixed carbon 24.85 %.

Figure 3. 1: Sieves and Grinder

3.2. Hydrothermal Treatment

A mixture of 50.0 g of coal and 150 ml of deionized water (except liquid amount analysis) was loaded into the 0.5L autoclave reactor (Parr-4843) and treated at different temperatures 150, 200, 250, 300 °C respectively for 30 minutes (except residence time analysis). The initial pressure of system was zero (except initial pressure analysis) and during the process the pressure of system was equivalent to the saturated steam pressure [17]. This autoclave was equipped with thermocouple, pressure meter and agitator. After loading the feed coal, the autoclave was sealed and then purged three times with nitrogen and the leak test was carried out. A heater was used for raising the temperature of slurry to desired temperature.

Figure 3. 2: Autoclave Reactor

The residence time of the each experiment is 30 minutes which means at each temperature, the coal is treated for 30 minutes, but it takes certain time (we call it reaching time) for reaching to desired temperature.

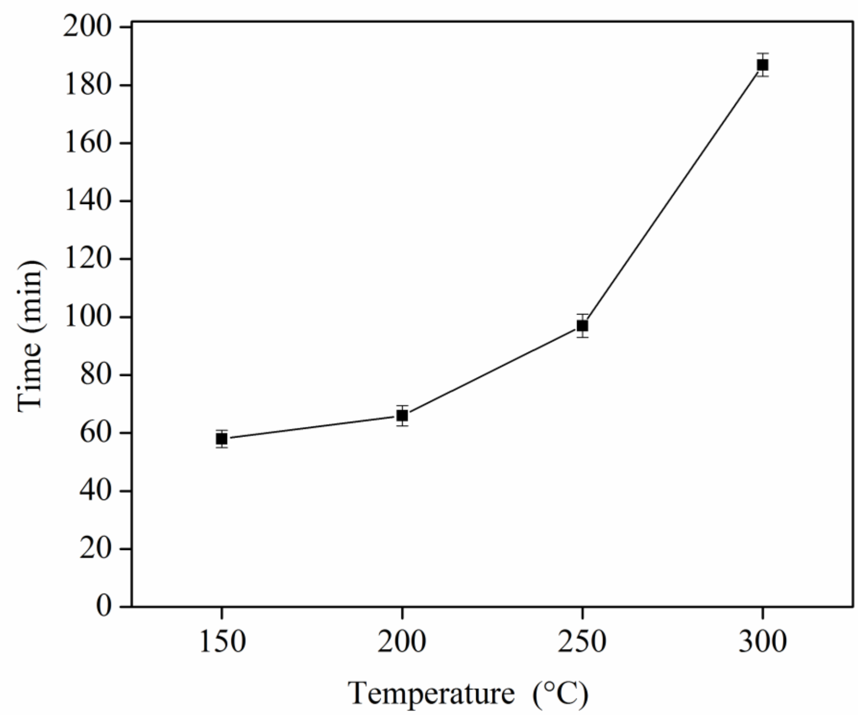

Figure 3. 3: Time-temperature profile for reaching the desire temperature

3.3. Filtration and Air Drying

After the treatment the reactor was cooled with water to room temperature and the produced gas was collected in a gas bag. The residue was a mixture of coal and water, the slurry was removed from reactor and filtered using a vacuum pump, a 0.1 µm filter paper was used for the filtration of the slurry. The liquor was collected in a glass bottle and used for various analyses.

After the filtration the solid part was wet thus for removing the moisture from the coal particles it was dried by air. The coal sample was kept in a container which had inlet and outlet for air, the flow rate of air was 5 l/min and the drying time by air was 20 hours. For regulating the pressure and avoiding the change in the flow rate, a regulator pressure and rotameter were used during the air drying.

3.4. Coal Characterization

Different analyses were performed for determining the characteristics of the raw and hydro-treated coal. Each analysis was carried out several times to get the reliable results.

3.4.1. Moisture analysis

A programmable muffle furnace (Model: F6020C-33-60) was used for moisture content of the coal utilizing ASTM D3173 [56] method. The temperature of the oven was set at 105 °C and the samples were heated at this temperature in crucibles for 1 hour, the loss of the samples weight represents the moisture content of the coal and was calculated using the following equation 3.1.

$$\boldsymbol{Moisture = \frac{W_0 - W_1}{W_0 - W_c}} \qquad \textbf{(3.1)}$$

Where the W_0 is the initial weight of samples plus crucible weight and W_1 is the weight of the sample after drying with oven plus crucible weight and W_c is the weight of crucible.

3.4.2. Ash analysis

Ash content of the coal samples were measured by utilizing the ASTM D3174 [57] method. Typically, in the first hour the temperature of the furnace was raised from room temperature to 450 °C, in the next hour it was raised to 750 °C for coal and then kept in isotherm for 2 hours, finally cooled to room temperature over the period of 3 to 4 hours. The residue of the samples represents the ash content of the coal and was calculated using the following equation 3.2.

$$\boldsymbol{Ash = \frac{W_1 - W_c}{W_0 - W_c}} \quad \textbf{(3.2)}$$

Where the W_0 is the initial weight of samples plus crucible weight and W_1 is the weight of the sample after drying with oven plus crucible weight and W_c is the weight of crucible.

3.4.3. Volatile matter analysis

The same as ash a programmable muffle furnace (Model: F6020C-33-60) was used. The volatile matter content of the coal samples were determined by utilizing ASTM D3175 [58] method. The operation temperature for volatile mater was 950 °C and the samples were heated at this temperature for 7 minutes in the furnace. The volatile matter was calculated using the following equation 3.3.

$$\boldsymbol{Volatile\ matter = \frac{W_0 - W_1}{W_0 - W_c} - Moisture} \quad \textbf{(3.3)}$$

Where the W_0 is the initial weight of samples plus crucible weight and W_1 is the weight of the sample after drying with oven plus crucible weight and W_c is the weight of crucible.

3.4.4. Fixed carbon analysis

Fixed Carbon was measured by subtracting the sum of moisture, ash and volatile matter from 100, utilizing the ASTM D3172 – 07a [59] method using the following equation 3.4.

Fixed carbon = 100 - (Moisture + Ash + Volatile Matter) (3.4)

3.4.5. Ultimate analysis

The ultimate analysis (C, H, N and S) of coal samples was determined by using an elemental analyzer (Model: Carlo Erba CHNS-O EA1108), based on D3172-07a [59] and D3176 – 09 [60] ASTM methods. 2 to 5 mg of samples was used in each experiment. For some experiments the samples were dried before the ultimate analysis.

Oxygen content was calculated by subtracting the sum of the nitrogen, carbon, hydrogen, sulphur and ash from 100 using the following equation 3.5.

Oxygen = 100 - (Nitrogen + Carbon + Hydrogen + Sulphur + Ash) (3.5)

3.4.6. Contact angle and penetration time

A drop shape analyzer (DSA10, Krüss) was used for measuring the water contact angle. Prior to measure the contact angle, a coal sample disc or pallet was prepared using about 400 mg of each sample, under high pressure (5000 psi). A droplet of water was added on the pallet, the process of the penetration of the droplet of water into the pallet was recorded and the contact angle at the first contact was measured. The time which the water droplet penetrates into the pallet was measured and is reported as penetration time.

3.4.7. Moisture reabsorption test

For moisture reabsorption test, a humidifier was used to create a saturated moisture chamber with a humidity of 95-99 % at temperature between 34-39 °C. A humidity meter was used for controlling the moisture content in the chamber. Two types analysis were carried out for testing moisture reabsorption ability:

1) All the samples were kept in the chamber and the weight of the samples after different interval of times was measured.
2) All samples were dried before the moisture reabsorption analysis for 1 hour at 105 °C, the samples were cooled to the room temperature in a desiccator, after that they were kept in the chamber and the weight of each sample was measured at different interval of times.

3.4.8. X ray fluorescence (XRF)

X ray fluorescence was used for determining the ash composition of raw and hydro-treated coal. Before the analysis, about 200 mg of each sample was used for making the pallet under high pressure (5000 psi). The analysis of XRF was conducted by department of chemical and materials engineering of university of Alberta.

3.4.9. FTIR

FTIR spectra for raw and hydro-treated coal were obtained by utilizing An ABB MB3000 Fourier Transformed Infrared. A resolution of 2 cm^{-1} and 100 scans were used for analyzing the samples. A low amount of each sample were used for analyzing and several times repeated for accuracy of the results. Horizon MBTM FT-IR software were used for proceeding the results.

3.4.10. SEM

SEM of raw and hydro-treated samples was done in the department of chemical and materials engineering of university of Alberta. A Hitachi S-2700 scanning Electron Microscope (SEM) equipped with a PGT IMIX digital imaging system and a PGT PRISM IG detector for Energy Dispersive X-Ray Analysis (EDX) was used taking the SEM images.

The SEM images were taken from raw and hydro-treated coal in different zooms, (x 300, x 2500, x 5000) for investigating the samples thoroughly.

3.4.11. TOC

About 15 mL of the filtrated liquid was used for determining the concentration of the organic carbon. The analysis was done by TOC analyzer, Shimadzu 5000A TOC analyzer and TOC-V CPH with TMN unit, in the biogeochemical analytical service laboratory of university of Alberta.

3.5. Measuring Organics and Inorganics in the Liquor

ICPMS and GCMS analysis were carried out for investigating the organic and inorganic component in the filtered liquor.

Organic compounds from the liquor were extracted with dichloromethane and trace amount of partially dissolved organic components were collected and analyzed by Varian CP 3800 gas chromatography with flame ionization detector and factor four capillary column (30 m ´0.25mm i.d.) and Saturn 2200 GC-MS ion trap spectrometer (Varian Inc., USA).

Inorganic components dissolved in the water were analyzed by ICPMS instrument in the department of earth and environmental sciences of university of Alberta.

3.6. Gas Chromatography

The collected gas was analyzed by the Agilent 7890A Gas Chromatograph with 8 feet, 1/8" HayeSep R stainless steel column. The flame ionization detector (FID) and thermal conductivity detector (TCD) detectors were used for determining the intensity of the compounds in the gas mixture. C_{1}-C_{5} method was used for analyzing the gas samples.

3.7. Initial Pressure of the Reactor

For increasing the initial pressure of the reactor nitrogen gas was purged into the reactor to get the desire pressure of 10, 20, 30 and 40 bar for the experiments.

All numbers for pressure are gauge pressures.

4. Chapter 4: Results and Discussion

4.1. Moisture of Raw and Hydro-Treated Coal

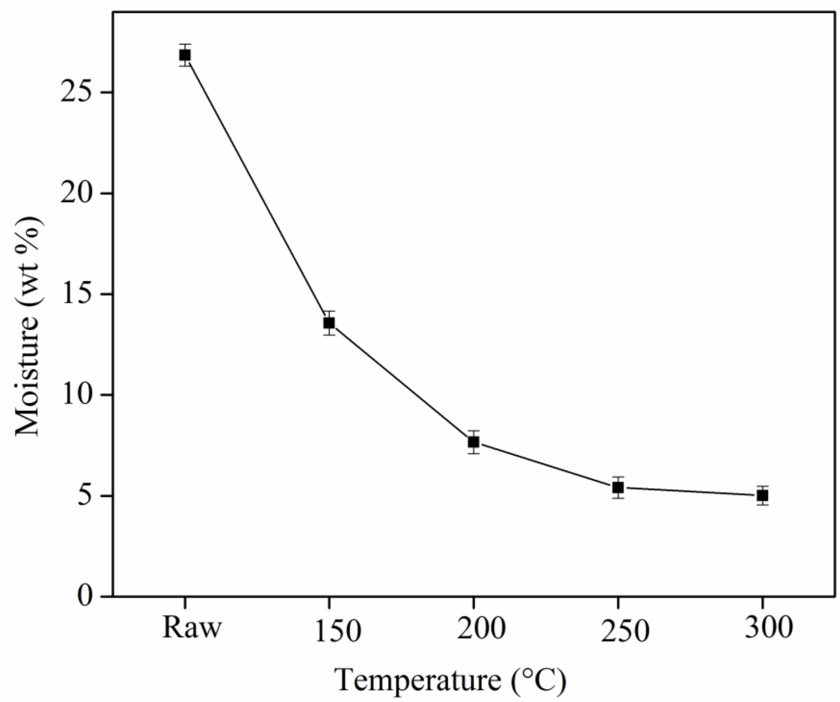

Figure 4.1: Effect of hydrothermal treatment temperature on moisture content of coal

Removal of moisture content of lignite coal is one of the main reasons for hydrothermal treatment. Figure 4.1 shows the effect of hydrothermal treatment on the moisture content of coal. In hydrothermal process the moisture is removed as liquid phase [17], by increasing the temperature, more functional groups break down and the pore structures of coal collapse leading to remove the moisture from coal [9]. Hydrothermal process was carried out several times in each temperature for more accuracy of the results. The raw coal (as-received) had a moisture content of 26.85 wt %. As seen in the plot there is a sharp decrease in moisture content of hydro-treated coal by increasing the temperature to 150 °C (13.57 wt %) and 200 °C (7.66 wt %), further increasing in temperature reduces the moisture content of coal but the rate of decreasing is not as high as before thus it is observed that the moisture content in 250 °C (5.41 wt %) and 300 °C (5.02 wt %) is very close to each other. Generally significant decrease in moisture content was observed by hydrothermal treatment especially at 250 °C and 300 °C. These results show high efficiency of hydrothermal treatment in dewatering of coal. The results of the moisture reduction agree with the results were reported by Laursen et al. [51].

4.2. Volatile Matter of Raw and Hydro-Treated Coal

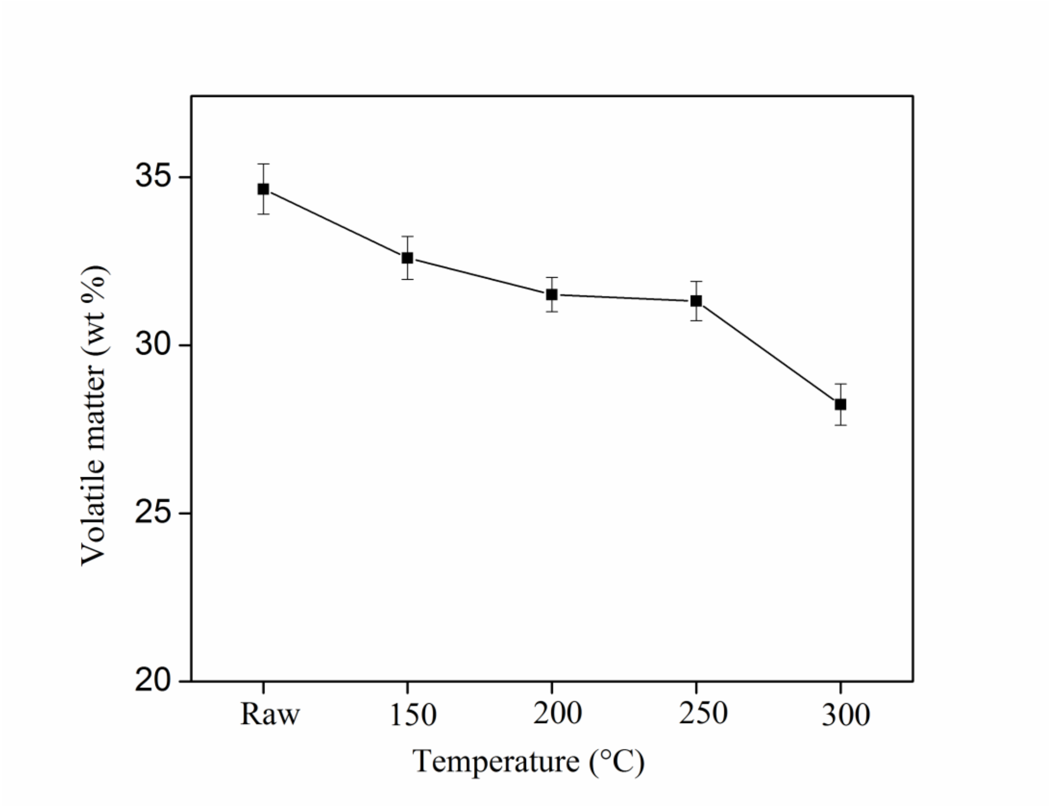

Figure 4.2: Effect of hydrothermal treatment on volatile matter content of coal (dry basis)

The amount of volatile matter content is affected by hydrothermal treatment. Usually the volatile matter content decreases during the hydrothermal treatment especially at high temperature due to the reduction of oxygen functional group. As seen in the Figure 4.2 the volatile matter content decreases by increasing the temperature of hydrothermal treatment. The initial amount of volatile matter was about 34.65 wt % (dry basis). Hydrothermal treatment at 150 °C decreases the volatile matter to 32.60 wt % (dry basis), by increasing the temperature, the coal lost more volatile matter during the process. At 250 and 300 °C the amount of volatile matter reached to 31.32 and 28.24 wt % (6.41 % less than the raw one) which signifies that vigorous pyrolysis occurred at high temperature [9]. Since volatile matter is favorable for combustion, losing too much volatile matter is not desirable for huge amount of coal thus depends on final application, treating at 250 °C may be more helpful for saving energy.

4.3. Ash Content of Raw and Hydro-Treated Coal

During the hydrothermal treatment some ash soluble part of coal dissolve in the water and leave the coal particles, this process decreases the ash amount, increases the higher heating value and reduces the problems dealing with high amount of ash [8, 17]. It has been observed in figure 4.3 by treating the raw coal which has 39.4 wt % db ash, there is a slight decrease in ash content of the treated coal at 150 °C (37.89 wt % db) and then ash amount increased slightly with the increase of temperature, at 200 and 250 °C the ash percentage is 39.06 and 40.16 wt %, and finally at 300 °C (41.89 wt %) exceed the ash percentage of the raw coal. It is clear that the ash content of coal cannot be increased during the hydrothermal treatment. This phenomenon can be explained by the loss of volatile matter at higher temperature, thus it is expected after 150 °C almost no change in ash content happens but due to decreasing of the volatile matter contents the percentage of ash increases.

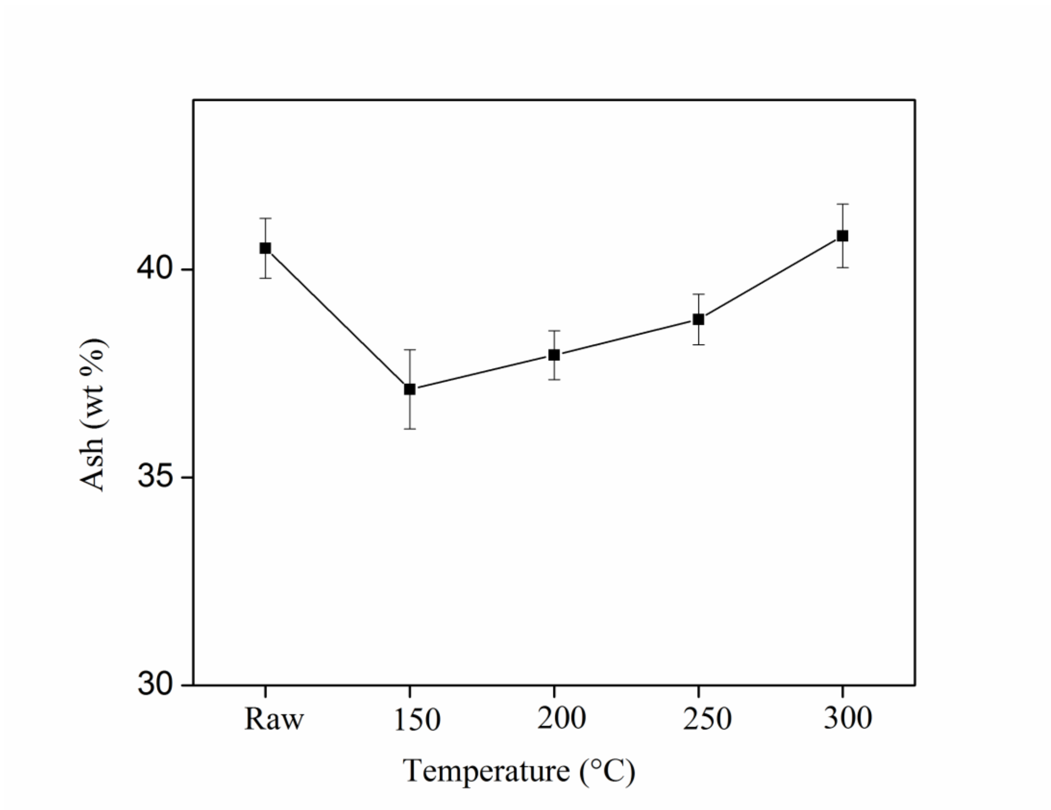

Figure 4.3: Effect of hydrothermal treatment on ash content of coal (dry basis)

4.4. Fixed Carbon of Raw and Hydro-Treated Coal

Coal components change by hydrothermal treatment and simultaneously fixed carbon content of coal also changes accordingly. As seen in the figure 4.4 the initial fixed carbon content of raw coal is 24.94 wt %. Because of the removal of the moisture and volatile matter during the hydrothermal treatment the percentage of the fixed carbon increases significantly and reaches to the 30.95 wt % at 300 °C.

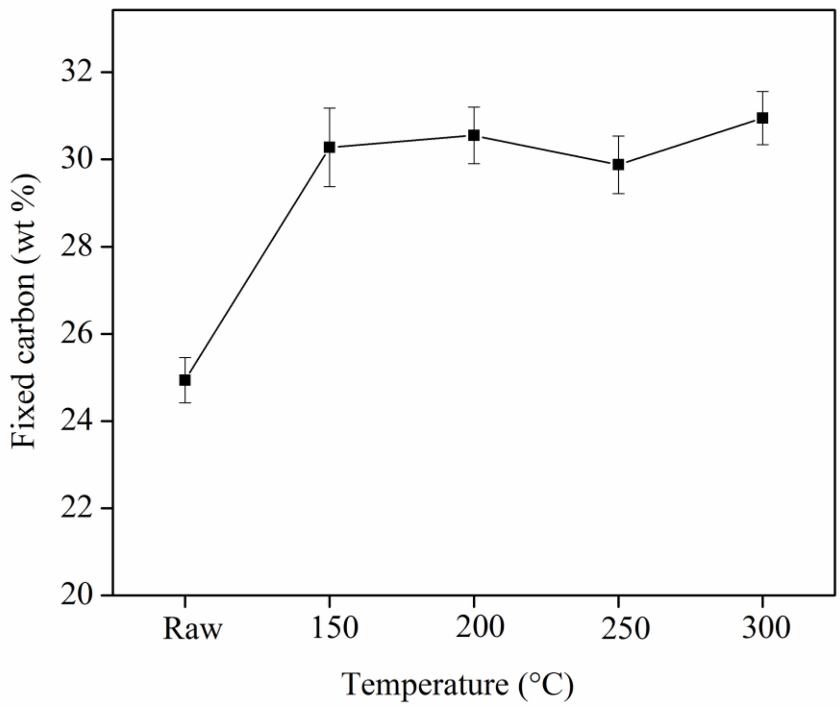

Figure 4.4: Effect of hydrothermal treatment on fixed carbon content of coal (dry basis)

4.5. Ultimate Analysis of Raw and Hydro-Treated Coal

During the hydrothermal treatment the elements of coal change, depend on the elements, it may increase or decrease. Table 4.1 shows that during the hydrothermal treatment almost there is a bit increase in the nitrogen percentage which is possibly due to reduction of the oxygen during the process. The carbon content increased significantly about 16.65 wt % shows the coal now is much more suitable for combustion and gasification. The hydrogen and sulphur content decreased but not significantly. Hydrogen decreased due to reduction of H_2O during hydrothermal treatment.

Table 4. 1: Effect of hydrothermal treatment on the ultimate analysis of coal (ash free basis)

	Raw	150 °C	200 °C	250 °C	300 °C
N (wt %)	0.72	0.86	0.95	1.04	1.01
C (wt %)	41.07	50.41	57.3	58.05	57.72
H (wt %)	5.72	4.88	4.96	4.74	4.55
S (wt %)	0.92	0.6	0.64	0.78	0.92
O (wt %)	51.57	43.25	36.15	35.38	35.8

By hydrothermal treatment the oxygen functional group of the coal such as hydroxyl and carboxyl break down and some organics leach out from coal to the water cause decreasing the oxygen content of coal [9, 10]. As it can be seen from table 4.1 the oxygen percentage of raw lignite coal is about 51.57 wt %. High percentage of oxygen content leads to high self-ignition tendency and lowering the hydrophobicity [4, 6], thus treating the raw coal is inevitable. Hydrothermal treatment decreases a huge amount of oxygen content during the process. At 300 °C the oxygen content reached to 35.80 wt % which shows high reduction of oxygen. But still there is this question that the reduction of oxygen content is due to breaking the oxygen functional group or removing the moisture of the coal?

For answering this question all the samples were dried in the oven at 105 °C for 1 hour to remove all moisture from the coal, after that the elemental analysis was carried out again.

Table 4. 2: Effect of hydrothermal treatment on the ultimate analysis of coal (daf basis)

	Raw	150 °C	200 °C	250 °C	300 °C
N (wt %)	1.14	1.20	1.13	1.29	1.33
C (wt %)	64.29	64.77	65.36	68.04	70.97
H (wt %)	4.95	4.83	4.75	4.91	4.97
S (wt %)	1.29	0.80	0.71	0.86	0.92
O (wt %)	28.34	28.41	28.06	24.90	21.80

The results presented in table 4.2 show the elemental analysis of coal on dry ash free basis. Table 4.2 shows the magnificent change of oxygen content percentage reducing from 28.34 to 21.80 wt %, based on these results it can be concluded that a part of oxygen content reduction is due to breaking of the oxygen functional groups such as hydroxyl and carboxyl.

As expected the carbon percentage of the treated coal was increased with the increase of treatment temperature. The carbon percentage of raw coal was 64.29 wt %, by hydrothermal treatment the carbon content increased to 70.97 wt %. High percentage of carbon, low percentage of moisture and oxygen at high temperature (250 and 300 °C) indicate that the lignite has truly upgraded and converted to a value added coal.

4.6. Higher Heating Value of Raw and Hydro-Treated Coal

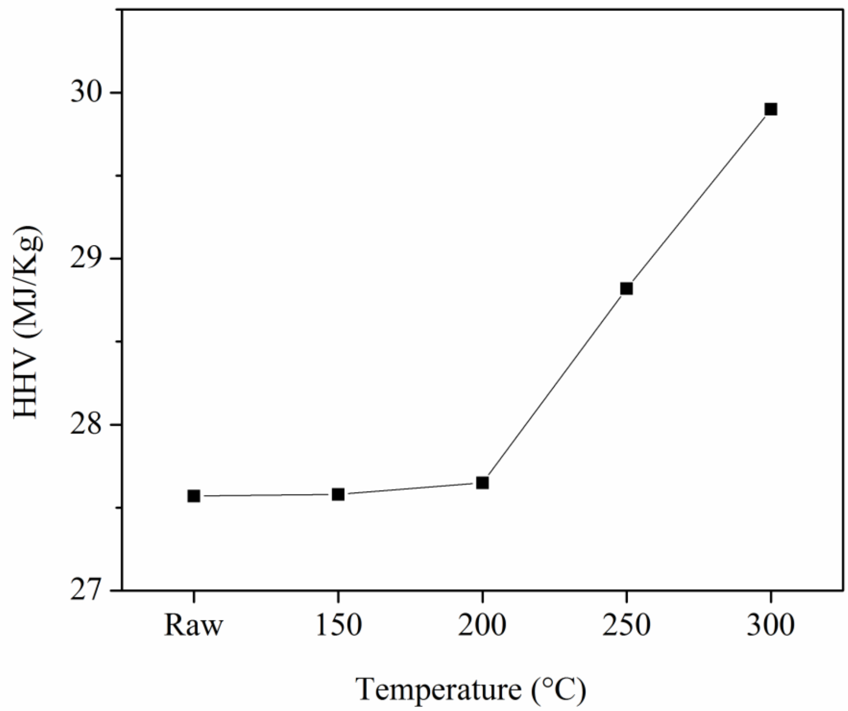

Figure 4.5: Effect of hydrothermal treatment on higher heating value of coal

The effect of hydrothermal treatment on the higher heating value (HHV) of coal was investigated. Equation 4.1 is used for calculating the higher heating value of raw and treated coal suggested by Neavel et al. [8].

$$\mathrm{GCV}\left(\frac{\mathrm{J}}{\mathrm{g}}\right) = 339.6\ \mathrm{C} + 1325.7\ \mathrm{H} - 12.53\ \mathrm{O} + 100.1\ \mathrm{S} - 14.7\ \mathrm{Ash} \quad (4.1)$$

For calculating the HHV of coal, weight percentage of each element is used. C stands for the weight percentage of carbon, H for hydrogen, O for oxygen and S for sulphur [8]. As seen in the table 4.2 the carbon and hydrogen content of treated coal increased and oxygen content of treated coal decreased by hydrothermal treatment. These changes cause increasing the higher heating value of coal. As seen in figure 4.5 the heating value of raw coal is 27.57 MJ/Kg, by hydrothermal treatment the HHV of treated coal increased and finally at 300 °C the HHV of coal reached to 29.90 MJ/Kg, which indicate an increase of 8.45 % in HHV.

4.7. Air Drying and Washing of the Coal

After the hydrothermal treatment the processed coal is in a mixture of the coal and water, the coal has to be filtrated and dried with the air thus air drying plays an important role in the process.

The effect of the air drying was investigated by measuring the moisture content of the coal in different time of the drying.

A flow rate of air with 5 lit/min was used for drying the coal. As seen in the figure 4.6 during the first 20 hours the rate of drying is faster than the rest, after that the drying rate decreases and finally around 45 hours it reaches to equilibrium which is the minimum moisture amount of the raw lignite coal. In addition the figure 4.6 can show the effect of the hydrothermal process in the removing moisture of the coal.

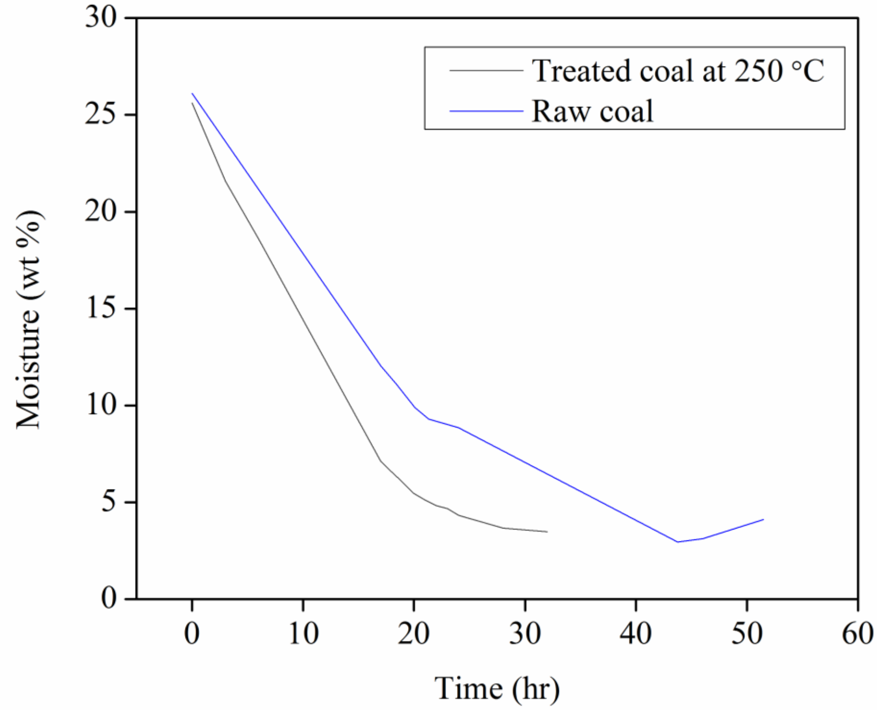

Figure 4.6: Effect of the air drying on moisture of the coal

In an experiment the moisture content of the hydro-treated coal (at 250 °C) before air drying was about 25 wt % showing the almost same moisture content as the raw coal, by 20 hours air drying the moisture content of the hydro-treated coal reached to about 5 wt % but for the raw coal it took 40 hours to reach to 5 wt %. This result shows that during the hydrothermal treatment the type of the moisture in the coal changes and moisture in the coal migrates to the surface of the coal which can be removed more easily.

Coal washing shows how much ash can be removed from the coal without considering the effect of hydrothermal treatment. The ash amount of the raw coal is about 35.1 wt % (dried basis) after the washing the coal in distilled water for 30 minutes the ash amount of the coal was about 34.4 wt %, it shows that temperature plays an important role in the ash removing from the coal.

4.8. Hydrothermal Condition

As known the water and batch reactor is used to prevent the evaporation of moisture during the process. Thus it is better to investigate the effect of the coal to water ratio on the hydrothermal treatment. Different amount of the water was used to study the effect of the coal / water ratio on the efficiency of the process in moisture removal.

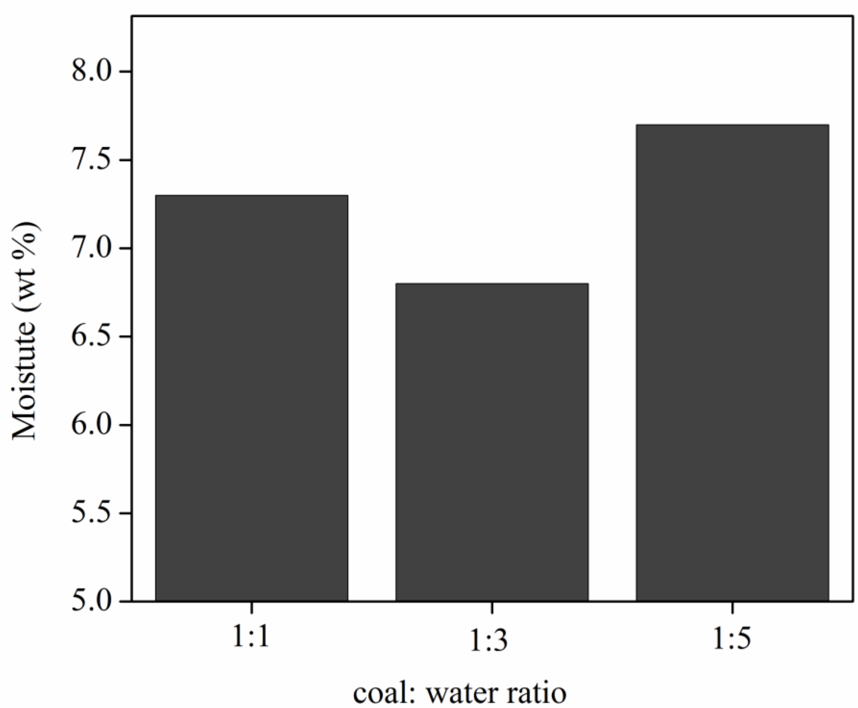

Figure 4.7: Effect of the coal / water ratio on the moisture

As seen in the figure 4.7 applying different amount of the water at 250 °C has negligible effect on the moisture content of the coal. It shows the amount of the water used in the hydrothermal process is not so much effective in the final product. The results of the ash content and elemental analysis of the coal (Appendix) for different amount of the water were the same.

For applying hydrothermal treatment in industrial scale a huge amount of the water has to be used, in this way providing the water and discarding the waste water can be a big problem. As known some organics and inorganics dissolve in the wastewater [8, 10] and make contamination, thus discarding the wastewater can make some environmental problems. In this case applying less amount of the water is a better idea to reduce the wastewater. Another idea is reusing of the wastewater as solvent in the process.

Reusing of the wastewater in hydrothermal treatment was investigated; a mixture of fresh water and waste water with the ratio of 1 : 2 was used in the batch reactor, the moisture content of hydro-treated coal by using the wastewater increased. The results of the moisture content can be seen in the appendix.

4.9. Contact Angle and Penetration Time of Raw and Hydro-Treated Coal

Wettability of coal is an important factor for storage, transportation, and preparation of coal water slurry (CWS) [4]. Contact angle measurement is one of the key techniques in wettability analysis. Contact angle depends on the bound force between water and the surface of coal. Therefore if the coal is hydrophilic the water droplet expands in the surface and it decreases the contact angle. Consequently, if the coal is hydrophobic the droplet of water almost keeps its spherical shape and the contact angle remains high. Non-polar material such as hydrocarbon is the main component of coal therefore it does not absorb the water that is known as a polar compound, but we have to consider that in low rank coal the oxygen functional groups which are polar are not as low as high rank coal and they decrease the contact angle [4].

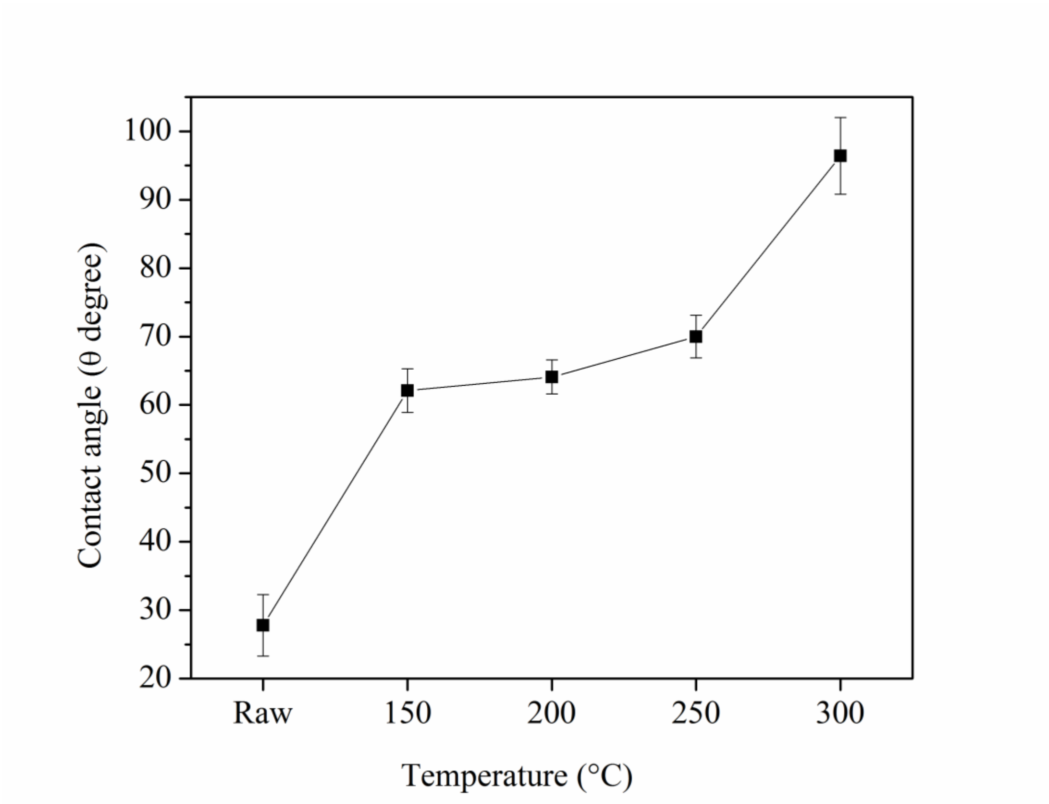

Figure 4.8: Effect of hydrothermal treatment on contact angle of coal

As the results show in the figure 4.8 the contact angle of the raw coal is 27.8 degree. Hydrothermal treatment can play an important role for reducing the oxygen functional groups in the coal and thus makes the coal more hydrophobic and increases the contact angle. As seen in the figure 4.2 and table 4.2 by increasing the temperature the volatile matter and oxygen content decrease therefore by decreasing these polar components, hydrothermal treatment makes the coal more hydrophobic. This agrees with results in figure 4.8 where the coal is more hydrophobic after treatment. There is a sharp increase in contact angle by treating the coal at 150 °C after that a slow increase in contact angle till 250 °C and finally at 300 °C the contact reaches to 96.4 degree indicates that the hydro-treated coal at this temperature is water repulsive. These results agree with the results reported by Yu et al. [4].

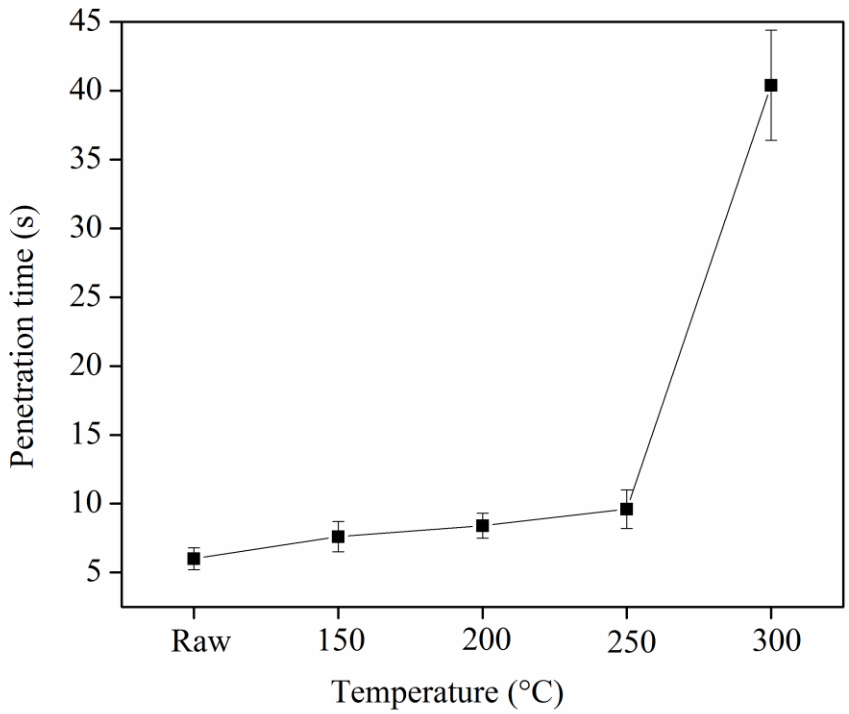

Figure 4.9: Effect of hydrothermal treatment on the penetration time of water in coal pallet

Based on the nature of the coal the penetration time of the water in coal can be different. For this purpose the pallets of raw and hydro-treated coal were investigated by putting a droplet of distilled water on the surface of the pallet and the time of the penetration water in the pallet was measured. Penetration time for the raw coal is relatively low due to having many hydrophilic groups. By hydrothermal treatment, penetration time increases. As seen in the figure 4.9 penetration time for raw coal is about 6 s, and for treated coal at 150 °C penetration time is 7.601 s showing less tendency of coal for absorbing moisture. At 300 °C it is observed that there is a sharp increase in the penetration time. During the experiment it was observed that the droplet of water stayed for a short time on the surface of the pallet after that it started to penetrate in the coal and this process took about 40.400 s which agrees with results of the contact angle measurement which there was a sharp increase in the contact angle at 300 °C. It can be concluded that there is a direct relation between contact angle and penetration time thus by increasing the contact angle the penetration time increases.

4.10. Moisture Re-Absorption of Raw and Hydro-Treated Coal

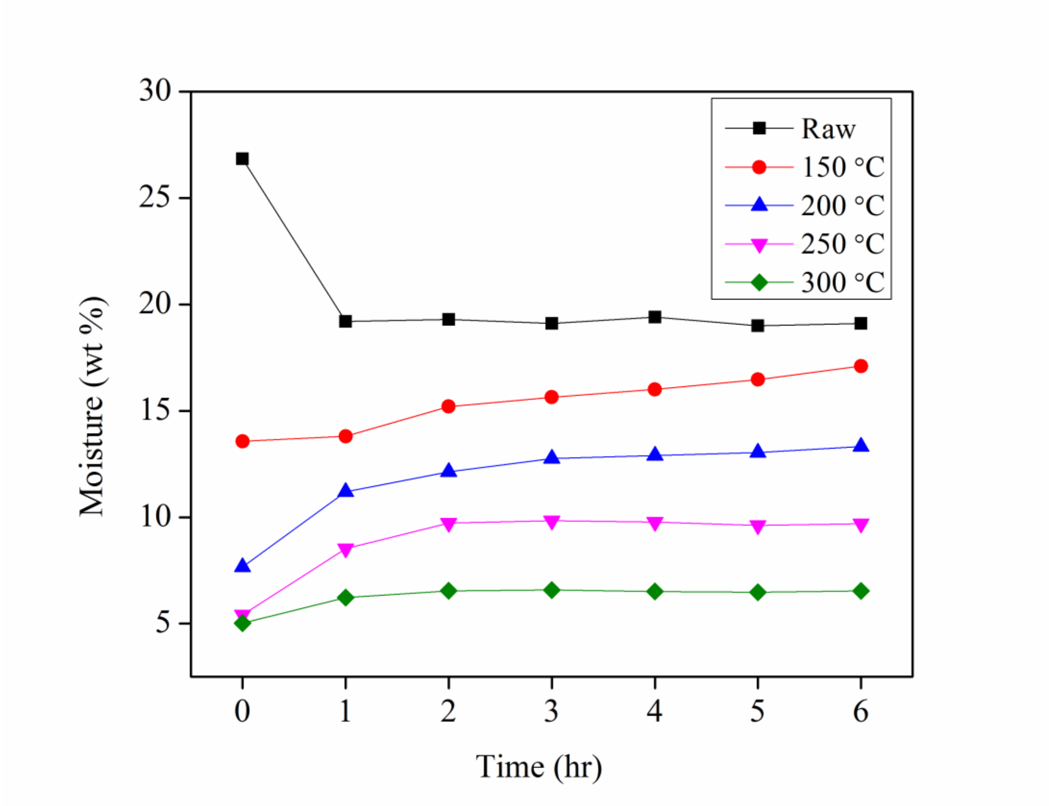

Figure 4.10: Effect of hydrothermal treatment on moisture reabsorption of coal

One of the main problems of low rank coal after drying is reabsorbing of moisture [27]. Absorption of moisture before and after hydrothermal treatment was also investigated during several hours. Reabsorption of moisture may occur after dewatering therefore the main purpose of dewatering of coal does not work properly, results with the loss of valuable time, energy and related cost. Hydrothermal treatment changes the property of the coal by shrinking the pore structure [8] of the coal and the organic matters extracted from coal generates an extra coating on the surface of coal particles [3] which prevents the reabsorption of moisture in the coal. For investigating the reabsorption ability of raw and hydro-treated coal, the samples were kept in a chamber with humidity of 95 - 99 % and the temperature of 34 - 39 °C. As seen in the figure 4.10 all samples absorbed moisture, except raw coal that lost moisture during the analysis which is probably due to having high amount of moisture content (26.85 wt %) and the temperature of the experiment. Observing the moisture absorbed by samples treated at 200, 250 and 300 °C which had almost the same initial moisture (7.66, 5.42 and 5.01 wt %) shows increasing the treatment temperature decreases the reabsorption ability of coal especially at 300 °C which the moisture reabsorption within 6 hours was only about 1.5 wt % shows very low tendency of coal for absorbing moisture after treatment.

It can be said in this analysis two factors are effective in reabsorption of moisture, first one tendency of coal for absorbing the moisture which depends on the nature of coal such as hydrophilic groups in coal, structure of coal and the second factor is the moisture content which functions as driving force. Certainly if the moisture content of the coal is high, absorbing moisture will be less, as seen in the figure 4.10, raw coal lost its moisture during the analysis and the moisture absorbed by coal treated at 150 °C is low which can be said is the effect of moisture content of coal.

For removing the moisture effect of coal and just studying the tendency of reabsorption ability of coal, the samples were dried in the oven at 105 °C for 1 hour for removing all the moisture, after that the reabsorption analysis was done again.

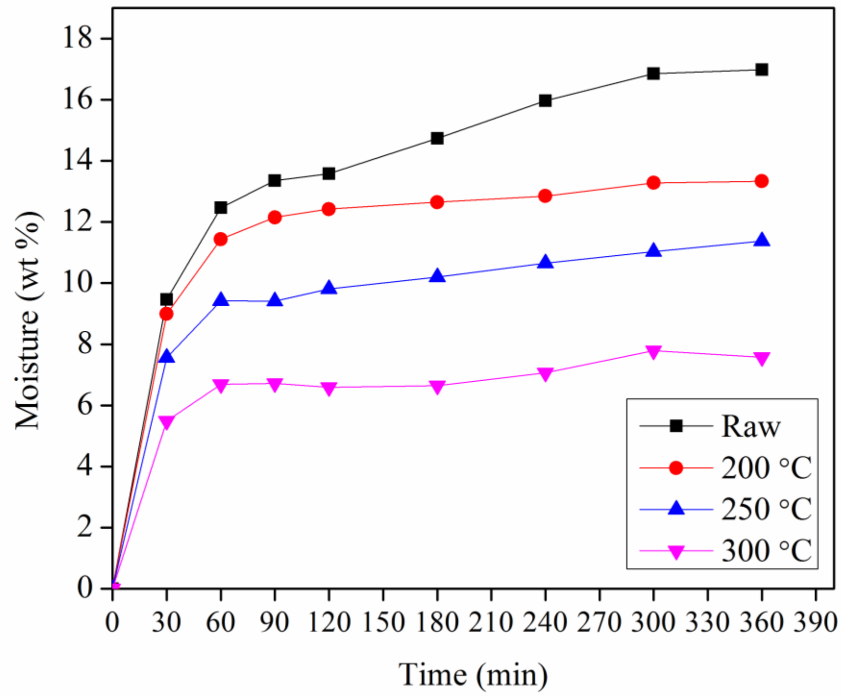

Figure 4.11: Effect of hydrothermal treatment on moisture reabsorption of dried coal

As seen in the figure 4.11 in this experiment all samples have absorbed moisture during the analysis thus the tendency of samples can be compared. The raw coal absorbed around 17 wt % moisture shows high tendency for absorbing the moisture, by hydrothermal treatment the tendency of moisture reabsorption decreased and less amount of moisture was absorbed in the same time, the coal treated at 300 °C just absorbed 7.5 wt % moisture during the experiment which indicates the hydrothermal treatment especially at high temperature can reduce moisture reabsorption tendency after drying.

4.11. Total Organic Carbon in the Filtrated Liquor

During the hydrothermal treatment, organic carbon are dissolved and transferred to the liquor thus the purification of the liquor before discarding it to the environment is necessary, in addition to that it causes the reduction of the valuable compounds during the hydrothermal process. Breaking the functional groups [9], losing the volatile and removing the moisture of the lignite during the hydrothermal process may cause transferring of the organic carbon to the liquid phase. Temperature of the process plays an important role in the increasing the concentration of TOC in the liquor. At higher temperatures especially at 250 and 300 °C the reduction of the moisture is high and the pyrolysis occurs more vigorously [9] thus it is expected the concentration of the TOC at higher temperature increases significantly. The results of the TOC can be seen in the figure 4.12.

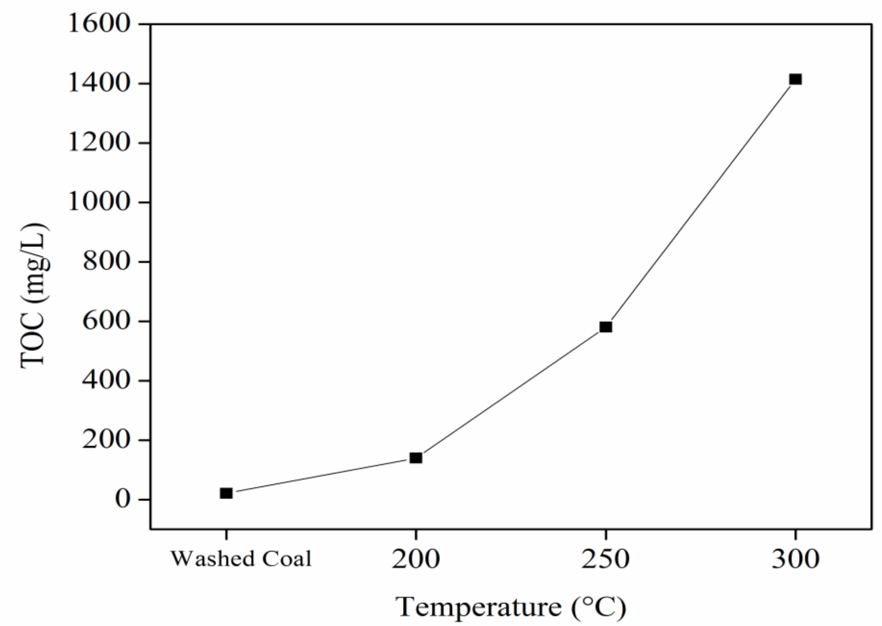

Figure 4.12: Effect of the hydrothermal treatment on the leaching of the organic carbon to the liquor

4.12. Liberation of Organics during Hydrothermal Treatment

Liberation of the organics during the hydrothermal treatment is a negative effect of this process. Organics are the materials which are favorable for combustion thus it is better to minimize the leaching out of the organics in the water. Table 4.3 shows the liberation of some organic matters during the hydrothermal treatment. Some organic matters partially dissolved in water under pressure and leached out of coal. The liquor generated from hydrothermal treatment at 300 °C was analysed by GCMS to investigate the effect of process on liberation of organics. The liquor was extracted with dichloromethane and trace amount of partially dissolved organic components were collected and analyzed by GCMS. It was observed that 85.831 wt % of liberated organics is Phenanthrene. The liberation of 3-Methyl-2-cyclopentenone and Naphthalene is around 2.096 and 7.58 wt % and total liberation of the rest is less that 5 wt %.

Table 4. 3: Effect of hydrothermal treatment on liberation of organics

Organic	Concentration (wt %)	Organic	Concentration (wt %)
Pyrene	0.361	Phenol	0.32
2,3-Dimethyl-2-cyclopentenone	0.444	2-Methylfuran	0.249
2-Methyl-2-cyclopentenone	0.584	4-Methoxyphenol	0.783
3-Methyl-2-cyclopentenone	2.096	Naphthalene	7.58
Methylnaphthalene	0.269	Phenanthrene	85.831
Anthracene	0.752	Fluoranthene	0.132

4.13. Liberation of Alkali Metals during Hydrothermal Treatment

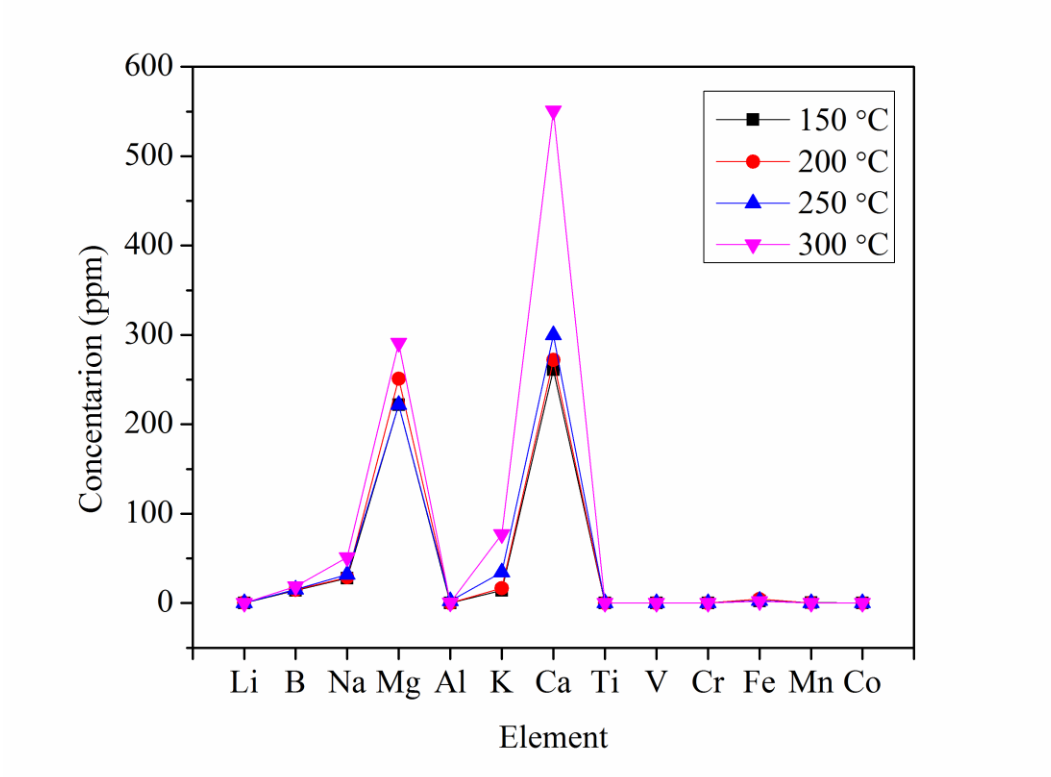

Figure 4.13: Effect of hydrothermal treatment on liberation of alkali metals

Figure 4.13 shows the liberation of alkali metals at different temperatures during the hydrothermal treatment. It has been observed that removal of these mineral matters increases with the increase of temperature, the concentration of the Ca in the liquor collected from hydrothermal treatment at 150 °C was about 250 ppm and in the liquor collected at 300 °C was about 550 pm which shows a high increase in concentration in liquor. The liberation of other elements such as Na, Mg and K was significantly and thus improved the quality of the hydro-treated coal.

4.14. Ash Component of Raw and Hydro-Treated Coal

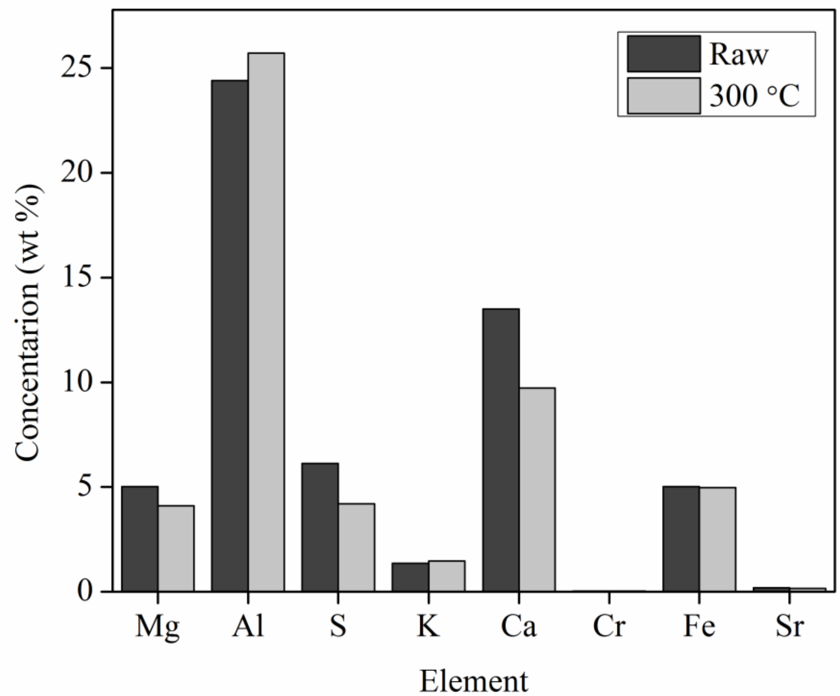

Figure 4.14: Effect of hydrothermal treatment on ash component of coal

Figure 4.14 shows the XRF analysis of the ash from raw coal and hydro-treated coal at 300 °C. It was observed that there is significant decrease in some alkali metals of ash such as Mg (5.03 to 4.11 wt %) , Ca (13.50 to 9.73 wt %) and some other elements such as S (6.12 to 4.21 wt %) and Fe (5.03 to 4.98 wt %). This result also agrees with the results of liberation of alkali metals in wastewater analyzed by ICPMS and ultimate analysis of coal.

4.15.FTIR Analysis of Raw and Hydro-Treated Coal

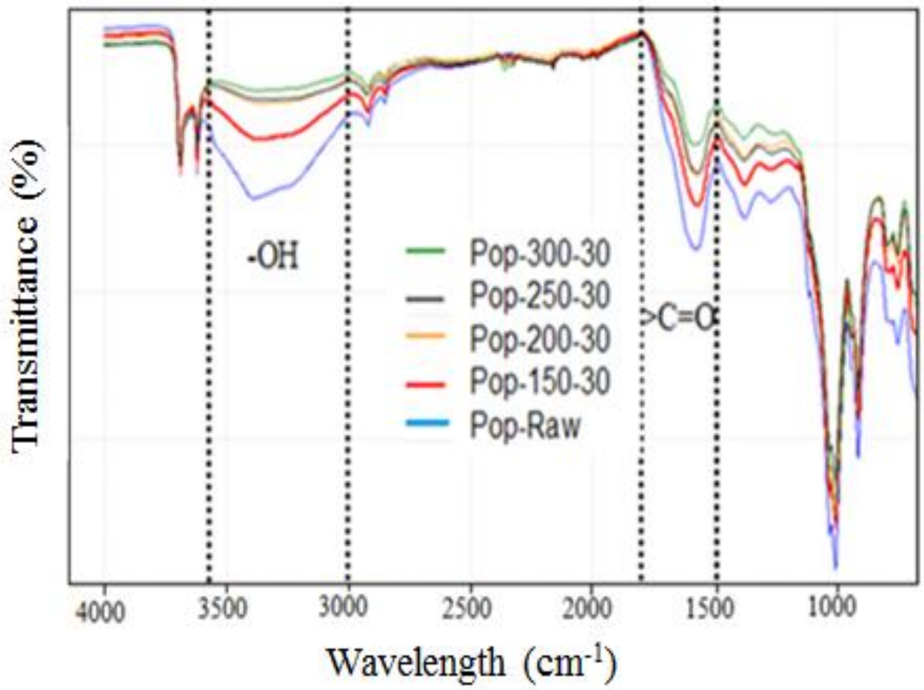

Figure 4.15: FTIR analysis

As mentioned earlier during the hydrothermal treatment the moisture content of coal decreases especially at high temperature, analysis was done by FTIR shows the same results. Figure 4.15 shows the FTIR analysis of the raw and hydro-treated coal, in this figure the intensity of peak between the wave number of 3050-3600 cm^{-1} shows the – OH group of the coal [9], as seen the raw coal has a broad peak indicating consisting high moisture, by increasing the treatment temperature the moisture content decreases thus the intensity of peak between 3050 - 3600 cm^{-1} decreases especially at 300 °C. The peak between 1400 - 1600 cm^{-1} indicating the C = O and COOM groups [9]. During the hydrothermal treatment some oxygen functional groups such as hydroxyl and carboxyl groups break [4, 9], the consequence of this process can be seen in the FTIR figure clearly by decreasing the peak between of 1400 - 1600 cm^{-1}.

4.16. SEM Analysis of Raw and Hydro-Treated Coal

During the hydrothermal treatment, the structure of coal changes significantly and the pore structure of coal collapses and tar covers the surface of the coal and blocks the pores [3, 8]. The morphology of the coal was investigated by SEM analysis.

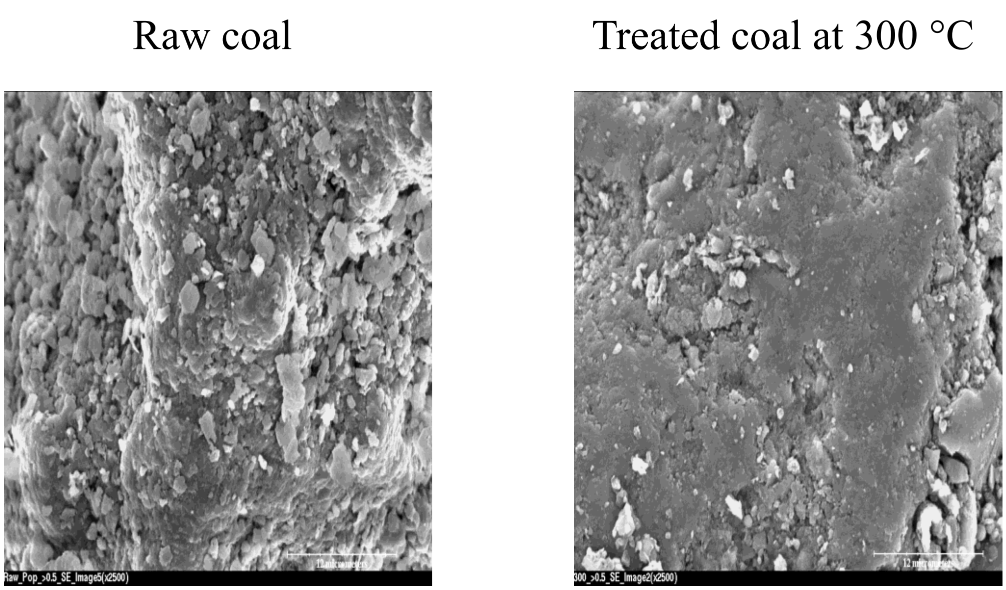

Figure 4.16: Physical property of raw and treated coal

These results show the changing of the coal structure by hydrothermal treatment. Visual inspection by SEM analysis shows hydro-treated coal has less porosity in comparison of the raw coal. During the process the coal particles changed to harder and more friable particles and in addition formation of larger particles were observed during the hydrothermal treatment [8]. The SEM results of the other hydro-treated coals are shown in appendix.

4.17. Gas Analysis of Raw and Hydro-Treated Coal

During the hydrothermal treatment the weak covalent bond breaks down and produces the CO, CO_2 and CH_4 during the hydrothermal treatment [52].

Table 4. 4: Gas analysis by Gas Chromatography

Component	200 °C	250°C	300 °C
Carbon dioxide (mol %)	7.15	15.63	61.31
Carbon monoxide (mol %)	0.1	1.02	2.37
Methane (mol %)	0.01	0.097	0.27
Propylene (mol %)	-	-	0.29

Gas analysis shows the elimination of major pyrolysis gases during hydrothermal treatment especially at high temperature. As seen in the table 4.4 by increasing the treatment temperature the amount of the CO_2, CO and CH_4 in the gas increases. The coal treated at 200 °C produced 7.15 mol % CO_2 in the process, drastic increase was observed when the treatment temperature was increased to 300 °C. By increasing the treatment temperature de-volatilization occurs more vigorously [9] which leads decreasing the oxygen content and extract more gas during the hydrothermal treatment. This result agrees with the figure 4.2 which shows drastic decrease in the volatile matter occurs when the treatment temperature increases to 300 °C.

4.18. Effect of the Size Fraction on Moisture and Ash Content

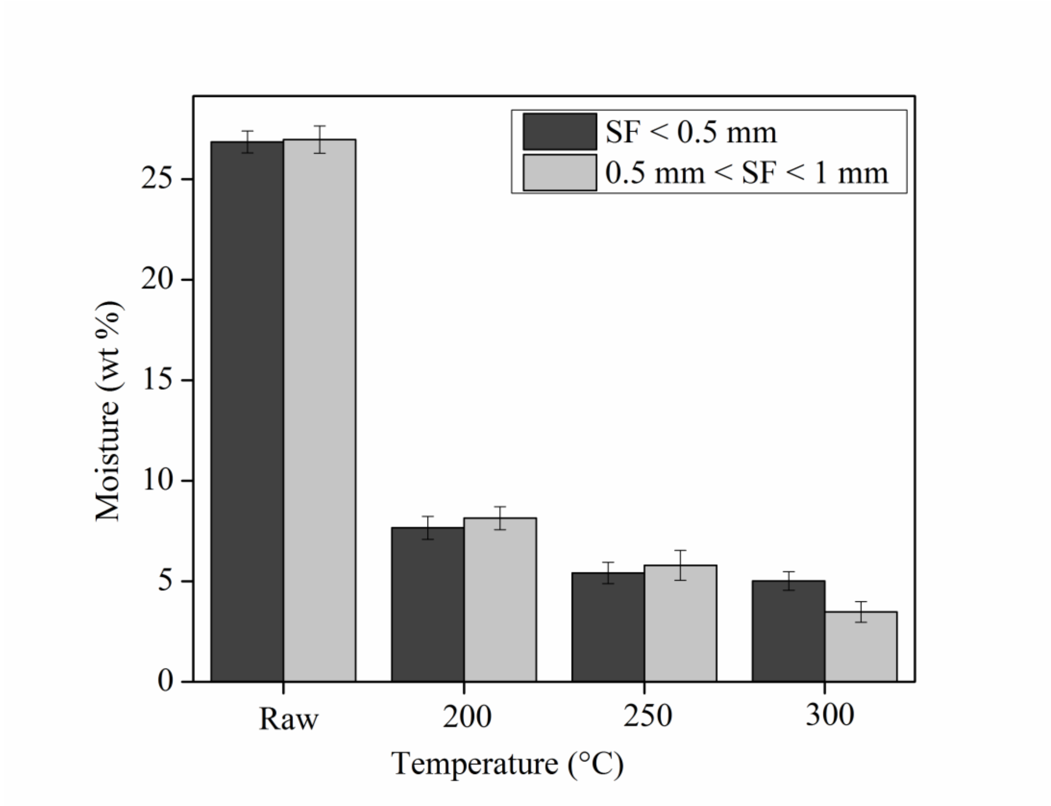

Figure 4.17: Effect of size fraction on moisture content of coal

Applying different size fractions of coal is one of the advantages of the hydrothermal treatment, usually final application determine the size fraction of coal [17]. Size fraction of coal changes the surface area contacted with water during the hydrothermal treatment. By decreasing the size fraction, more surface area contacts with water thus the efficiency of the process has to be higher. Hydrothermal treatment was done for two size fractions < 0.5 mm and 0.5 – 1 mm under the same treatment conditions. It was expected with less size fraction the moisture reduction increases but as seen in the figure 4.17 there is almost no change in the moisture content of treated coal thus this question rises, why the effect of size fraction can’t be seen?

The residence time of treatment at each temperature is 30 minutes, we have to consider that in addition of this 30 minutes, a certain time takes to reach to desire temperature. As seen in figure 3.3 for reaching to 150 °C it takes 58 minutes and for reaching to 300 °C, it takes 187 minutes thus the process time of hydrothermal treatment for each temperature is more than 30 minutes. During this long process time the moisture of the coal does not change by changing the size fraction. Effect of changing the size fraction on the ash content was also investigated and similar results were achieved.

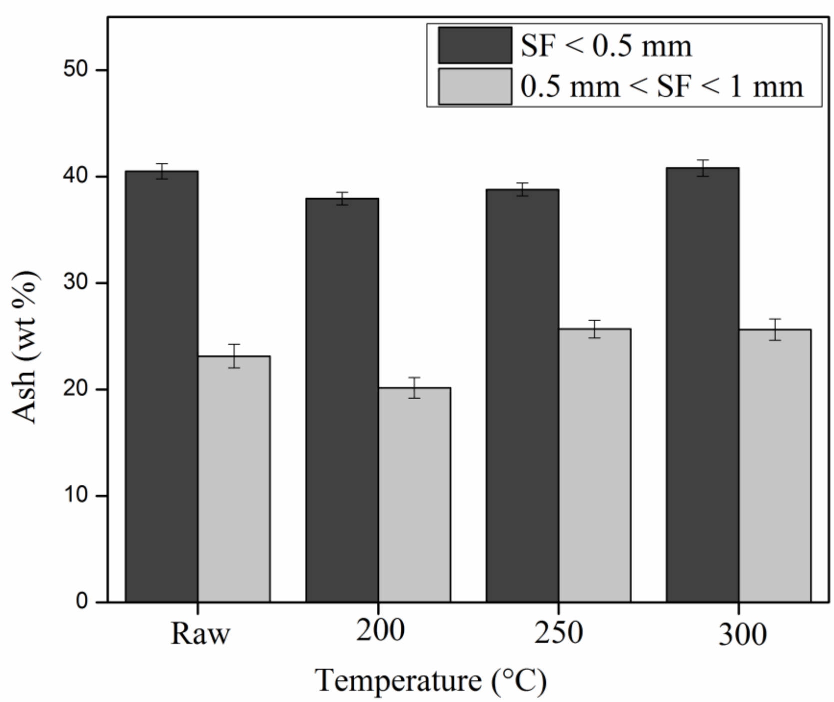

Figure 4.18: Effect of size fraction on ash content of coal (dry basis)

In this experiment the raw coals which were used for hydrothermal treatment had different amount of ash. As seen in the figure 4.18 the raw coal for size fraction between 0.5 – 1 mm has ash content of 23.14 wt % and the raw coal for size fraction less than 0.5 mm has the ash content of 39.4 wt %. The results show that the reduction of ash follows the same trend in both size fractions which shows that the size fraction is not effective in reduction of ash. Possibly by reducing the process time the effect of the size fraction on the moisture and ash content of coal can be seen.

4.19. Effect of Residence Time

4.19.1. Effect of residence time on moisture and ash content

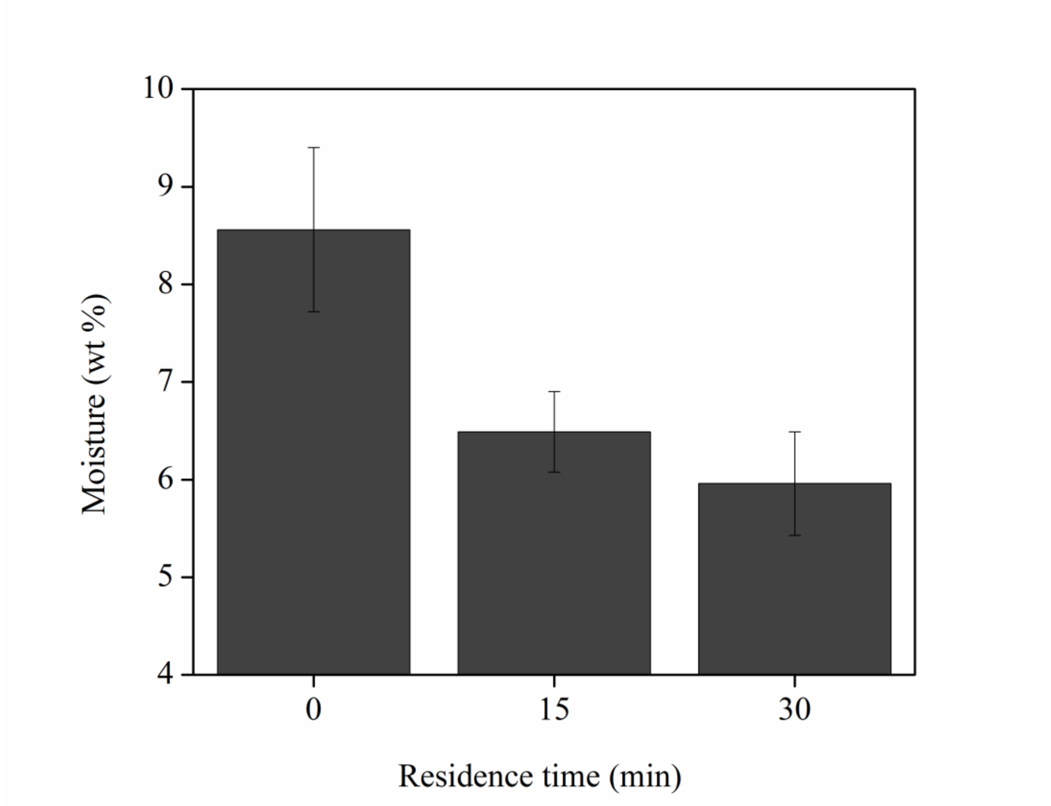

Figure 4.19: Effect of residence time on the moisture content

It was observed that the temperature of the treatment has a significant influence on the moisture and other properties of coal. As seen in the figure 4.1 by changing the temperature, the moisture amount changes remarkably. It is important to know the effect of the residence time on the removal of moisture from the coal, in this way the best time for hydrothermal treatment can be found. As seen in the figure 4.19 the moisture content of raw coal in about 26 wt % , hydrothermal treatment was done in 3 different residence time (0, 15 and 30 minutes). Hydrothermal treatment with 0 minutes residents' time decreases the moisture content of coal to 8.5 wt %. Maybe this question rises, how the moisture content decreases if the residence time is 0 minute?

As mentioned earlier for each temperature it takes a certain time to reach to the desire temperature, for 250 °C, it takes about 96 minutes thus hydrothermal treatment was done at temperature of 25 – 250 °C for 96 minutes.

By increasing the resident time to 15 and 30 minutes the moisture content reduced to 6.5 and 5.5 wt % which shows by 15 minutes process time, almost hydrothermal treatment is complete and further process may not be required.

The effect of the changing time on the ash content of coal was investigated. As seen in figure 4.20 changing the residence time has almost no effect on the ash content of hydro-treated coal. The ash content of the coal treated with 0 minutes residence time is about 34.46 wt % and the ash content for 30 minutes residence time is 35.01 wt % showing negligible effect of residence time thus it is better to carry out the hydrothermal treatment with the less residence time.

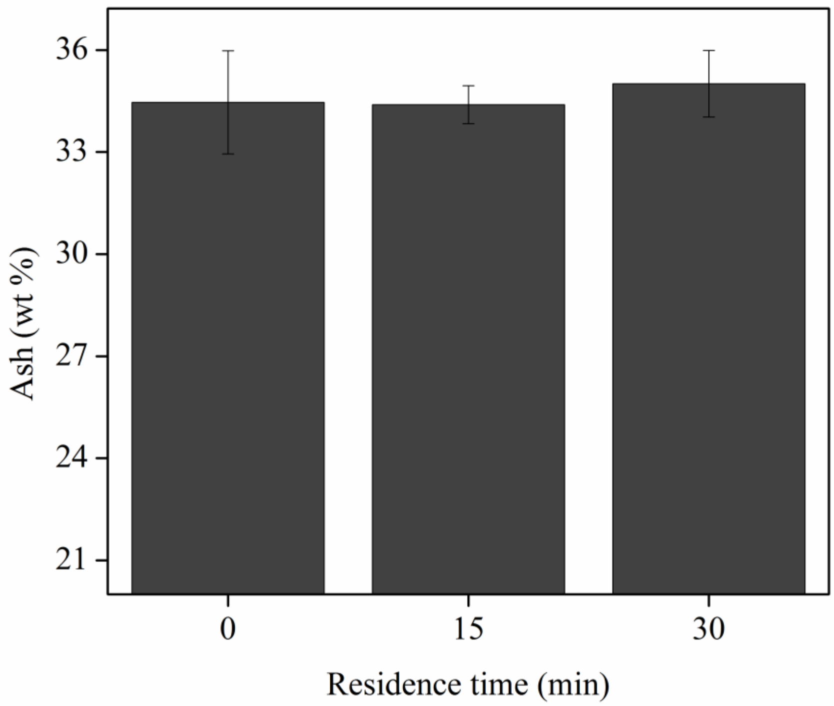

Figure 4.20: Effect of residence time on the ash content (dry basis)

4.19.2. Effect of residence time on elemental analysis of coal

Since treatment temperature has some effects on the ultimate analysis of the coal, residence time may affect the ultimate analysis of the coal as well. Probably if we can decrease the ramping time to reach the desire temperature, the overall process time will decrease and changing in properties of the hydro-treated coal by changing the residence time can be seen better. As seen in the table 4.5 increasing the residence time increases the carbon percentage of the coal, by 0 min treatment the carbon content of the coal is about 66.81 wt % (daf basis), by increasing the residence time of the process to 30 minutes, the carbon content reached to 69.66 wt %. Due to pyrolysis in the coal, the oxygen content of the coal decreases.

When the residence time increases the pyrolysis takes longer and more oxygen content removed from the coal which reduces the reactivity and increases hydrophobicity of the coal. By 0 minute treatment the oxygen content was 26.61 wt % (daf basis) and by 30 minutes of the process the oxygen content reached to 23.65 wt %.

Table 4. 5: Effect of the residence time on the ultimate analysis of the coal (daf basis)

	0 min	15 min	30 min
N (wt %)	0.92	0.99	1.00
C (wt %)	66.81	69.00	69.66
H (wt %)	4.49	4.59	4.64
S (wt %)	1.17	1.05	1.05
O (wt %)	26.61	24.38	23.65

4.20. Effect of Initial Pressure

4.20.1. Effect of initial pressure on saving energy in hydrothermal treatment

So far all experiments were done based on zero initial pressure and the pressure during the process was equivalent to saturated pressure [17]. As mentioned earlier for each temperature it takes certain time to reach to desired temperatures. If this time can reduce, the hydrothermal treatment can be more cost effective.

The main idea of hydrothermal treatment is removing the moisture as liquid phase thus the latent heat of water can be saved [4]. Regarding this issue the hydrothermal treatment were done in a batch autoclave reactor to prevent evaporation of water, though it is expected a low amount of water evaporates by using zero initial pressure thus if the initial pressure increases, the evaporation of water is prevented and all the energy is consumed for increasing the temperature of the slurry hence the reaching time to desired temperature will be less.

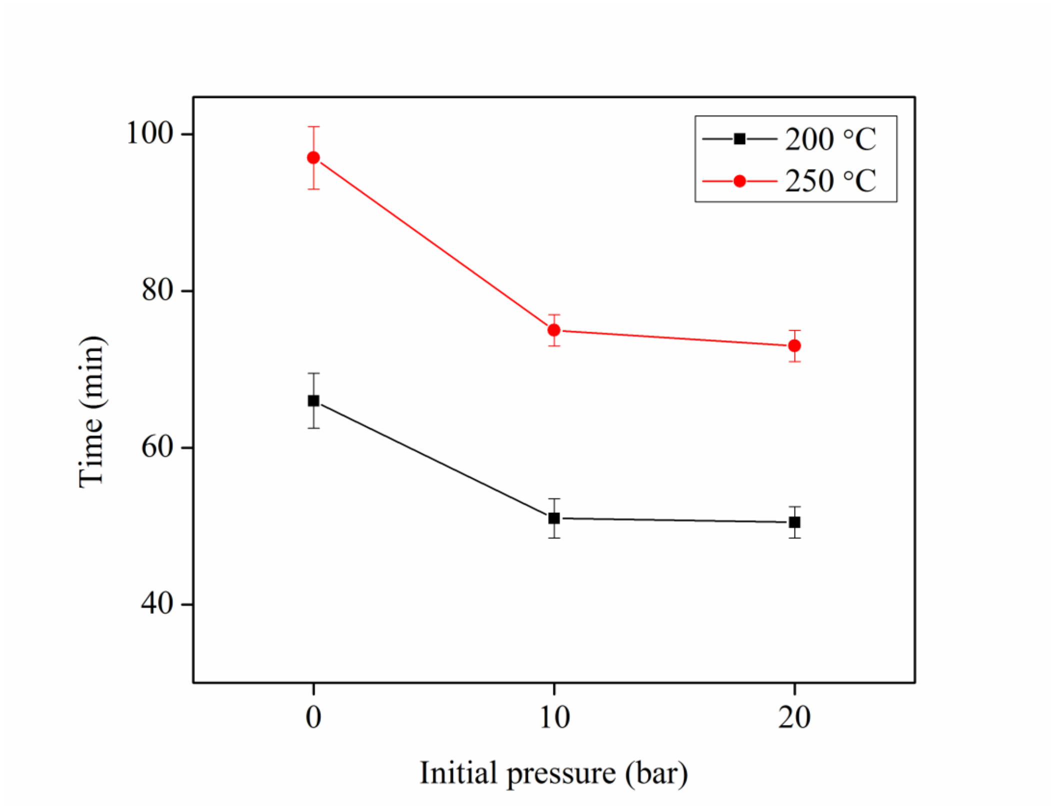

Figure 4.21: Effect of initial pressure on reaching time to desire temperature

As seen in the figure 4.21 for two different temperatures hydrothermal treatment was done in 3 different initial pressures (0, 10, 20 bars). It is observed that as expected the time takes to reach to 200 and 250 °C was less. It takes almost 66 and 97 minutes to reach to 200 and 250 °C with 0 bar initial pressure, by increasing the initial pressure to 10 bar, a significant decrease was observed. It takes about 51 and 75 minutes for reaching to 200 and 250 °C. By further increasing the initial pressure to 20 bar the reaching time decreased to 50 and 73 minutes. It seems further increasing of initial pressure has no significant impact on the ramping time, for proving this, two more experiments with initial pressure of 30 and 40 bar at 200 °C were carried out.

Figure 4.22 is a good proof that increasing the initial pressure more than 10 bar does not make significant change.

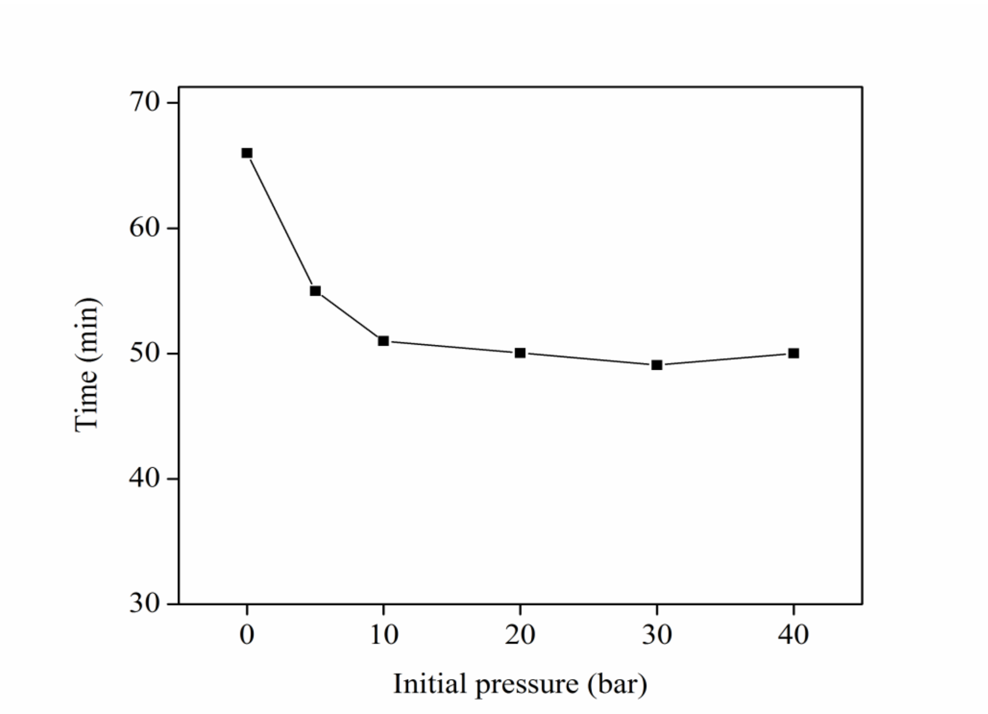

Figure 4.22: Effect of initial pressure on reaching time to desire temperature

4.20.2. Effect of initial pressure on the moisture and ash content

Changing the initial pressure has some effect on the properties of the final product.

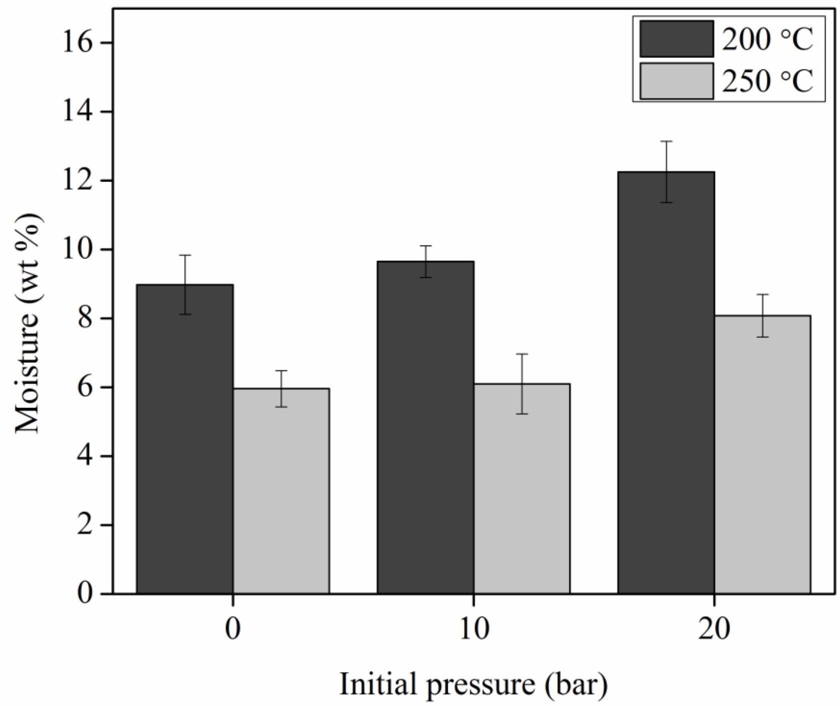

Figure 4.23: Effect of the initial pressure on the moisture content of the hydro-treated coal

During hydrothermal treatment the moisture in the coal absorbs the energy, and its kinetic energy increases thus it leaves the coal as a liquid phase. As seen hydrothermal treatment is an efficient way for decreasing the moisture content. Increasing the initial pressure helps to decrease the ramping time to desired temperature but as seen in the figure 4.23 the ability of hydrothermal treatment in reducing moisture decreases. Different initial pressures (0, 10 and 20 bar) in two different temperatures were applied to see the effect of the initial pressure on the moisture content of the coal. The initial moisture content of the coal was about 26.5 wt %, by applying 0 bar initial pressure the moisture content of hydro-treated coal was about 9 and 6 wt % at 200 and 250 °C, increasing the initial pressure to

10 bar increase the moisture content to 9.6 and 6.1 wt % and finally by applying the 20 bar as initial pressure the moisture content reached to12.2 and 8.1 wt % which shows a high increase in moisture content by increasing the initial pressure from 10 to 20 bar.

Changing the initial pressure had no effect in ash content of hydro-treated coal in both temperatures (200 and 250 °C).

Ash content of the coal by applying the 0 bar initial pressure was about 34.44 and 35.01 wt % at 200 and 250 °C and by increasing the initial pressure to 10 and 20 bar the ash content almost had no change.

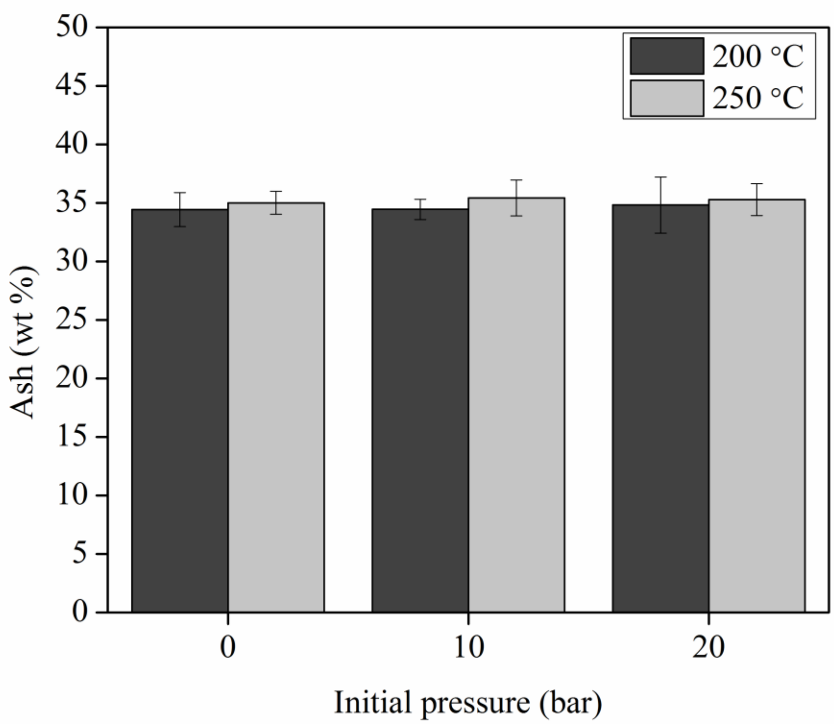

Figure 4.24: Effect of the initial pressure on the ash content (dry basis) of the hydro-treated coal

By considering the positive effect of the increasing the initial pressure on the ramping time and its negative effect on the moisture content, it is better to apply 10 bar as initial pressure where decreasing the ramping time is significant and increasing the moisture content of the coal is not considerable.

4.20.3. Effect of initial pressure on yield of the product

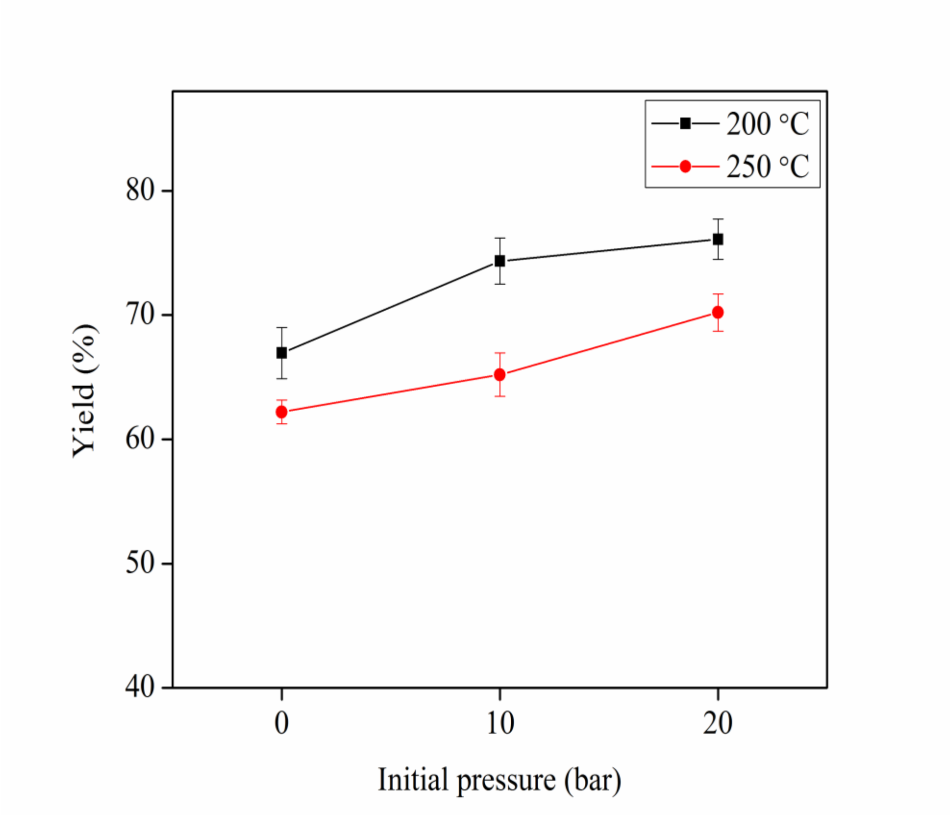

Figure 4.25: Effect of initial pressure on yield of the product

During the hydrothermal treatment some compounds such as moisture, ash, volatile and mineral matters are removed from the coal. Increasing the initial pressure affects the amounts of the compound which are removed from coal and leads to achieve more products finally. Here the final weight of the treated coal was measured and was divided by the initial amount of the coal (50 g) to achieve the yield. As seen in figure 4.25 the yield of the hydrothermal treatment with 0 bar initial pressure is about 62 and 67 % at 200 and 250 °C respectively. By increasing the initial pressure the yield of product increases and finally by applying the 20 bar as initial pressure, the yield of product reached to 70 and 76 % which shows a magnificent increase in product, but we have to consider that by increasing the initial pressure the moisture content of the coal increases thus for seeing the effectiveness of the increasing of the initial pressure on yield of the product we have to eliminate the effect of the moisture.

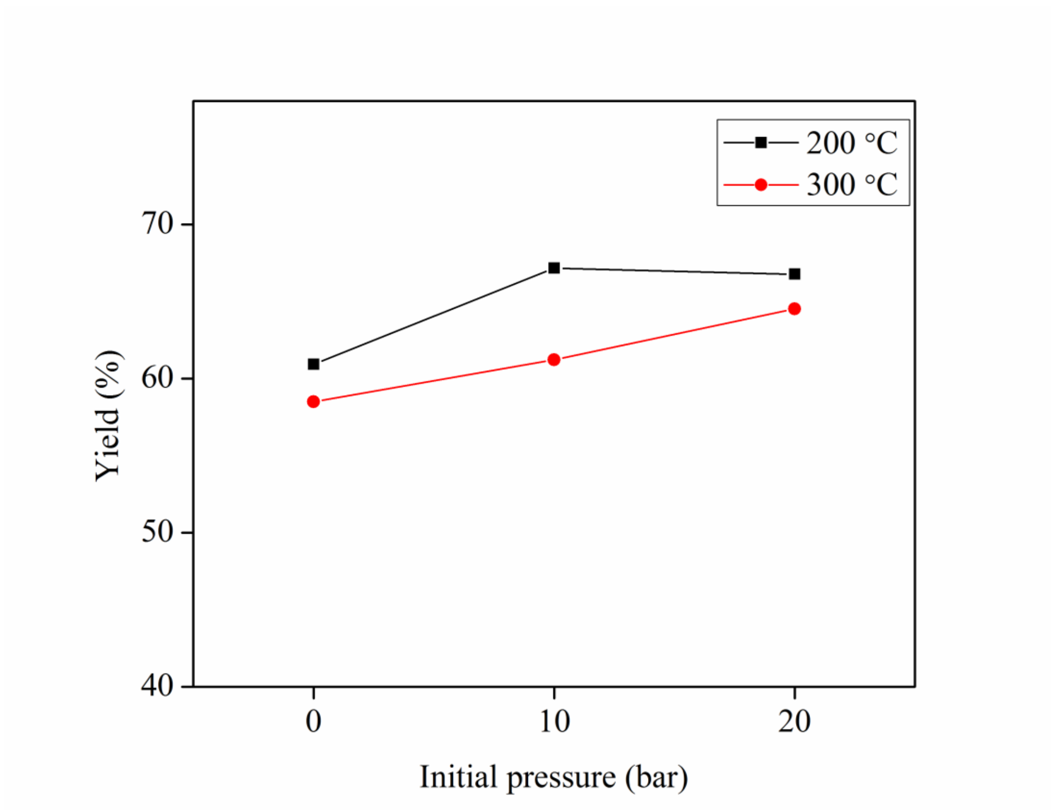

Figure 4.26: Effect of initial pressure on yield of the product (dry basis)

As seen in figure 4.26 after eliminating the effect of the moisture still the yield of the product increases and as was shown in figure 4.24 the ash content of hydro-treated coal with different initial pressure was the same thus it can be concluded that the loss of volatile which is favorable for combustion is less with increasing the initial pressure.

4.20.4. Effect of the initial pressure on the coal elements

Effect of the initial pressure on the ultimate analysis of the coal was investigated. The elemental percentage of the coal samples treated at 250 °C with different initial pressure was measured.

Table 4. 6: Effect of the initial pressure on ultimate analysis (daf basis)

	0 bar	10 bar	20 bar
N (wt %)	1.00	0.99	1.01
C (wt %)	69.66	68.92	69.12
S (wt %)	1.05	1.04	1.06
H (wt %)	4.64	4.57	4.57
O (wt %)	23.65	24.47	24.24

As seen in table 4.6 increasing the initial percentage decreases the carbon percentage, the carbon content in the coal sample treated by applying 0 bar initial pressure is 69.66 wt % (daf basis), increasing the initial pressure to 20 bar decreases the carbon percentage to 69.12 wt %. As mentioned in section 4.20.3 by increasing the initial pressure the loss of volatile matter decreases which means by applying higher initial pressure, de-volatilization occurs less vigorously, consequently loss of the oxygen content is less, this agrees with results of the oxygen content in table 4.6 which shows by increasing the initial pressure from 0 to 20 bar the oxygen content increased from 23.65 to 24.24 wt %.

4.21. Comparison the Energy Required for Hydrothermal Treatment and Thermal Drying

It is important to know how much energy is needed for the hydrothermal process and compare it with thermal drying. The energy required for treating at 150, 200, 250 and 300 °C was calculated. It was assumed that in the hydrothermal treatment there is no evaporation of water [4]. The energy required for process can be divided into three categories. The energy required for raising the temperature from room temperature to desired temperatures, the heat loss during the raising the temperature and the energy required for keeping at desire temperature for 30 minutes. Specific heat of the coal is considered constant during the process (C_p = 1.6 kJ/kg) and specific heat of the water changes by changing the temperature. It is assumed that 50 g of coal and 150 ml of water is used for the process. The diameter of the reactor is 10 cm and height of it is 19 cm

In thermal drying it is assumed that the temperature of 50 g coal consisting 26 wt % moisture is raised from room temperature to 105°C, then kept 1 hour at this temperature for removing the moisture after that the temperate of coal is increased to desired temperature, the heat loss during the raising of the temperature and removing the moisture was calculated.

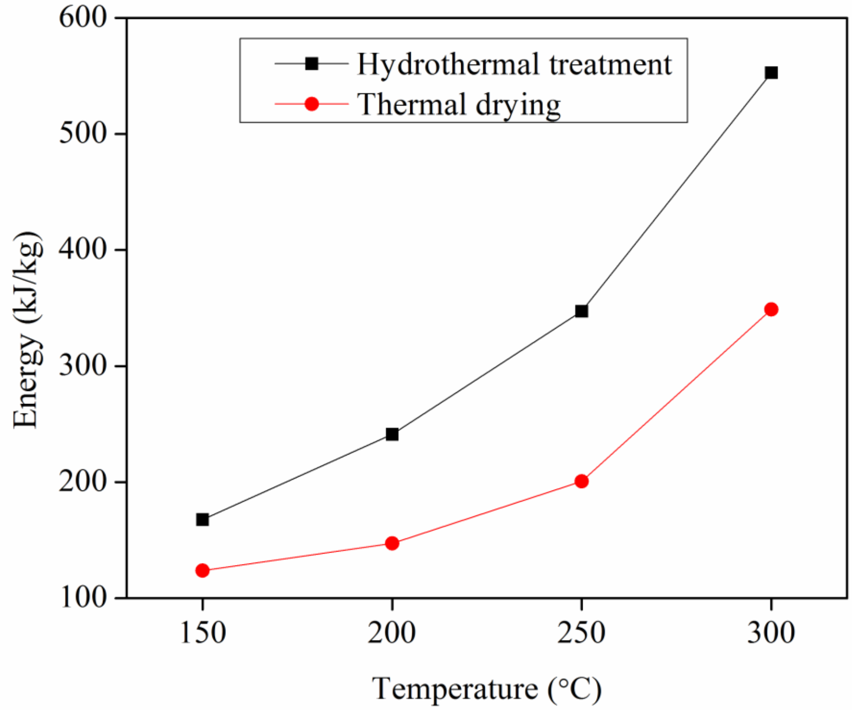

Figure 4.27: Energy required for hydrothermal treatment and thermal drying

A simple comparison between hydrothermal treatment and thermal drying shows, more energy is required for hydrothermal process. Thus somehow the energy required for the process has to be decreased. For this purpose it is assumed we can recycle the wastewater and it can enter to the reactor at 50 °C below the desired temperatures, then the required energy is calculated. Figure 4.28 shows the required energy for the process. High reduction in required energy is observed and in comparison with the thermal drying less energy is required.

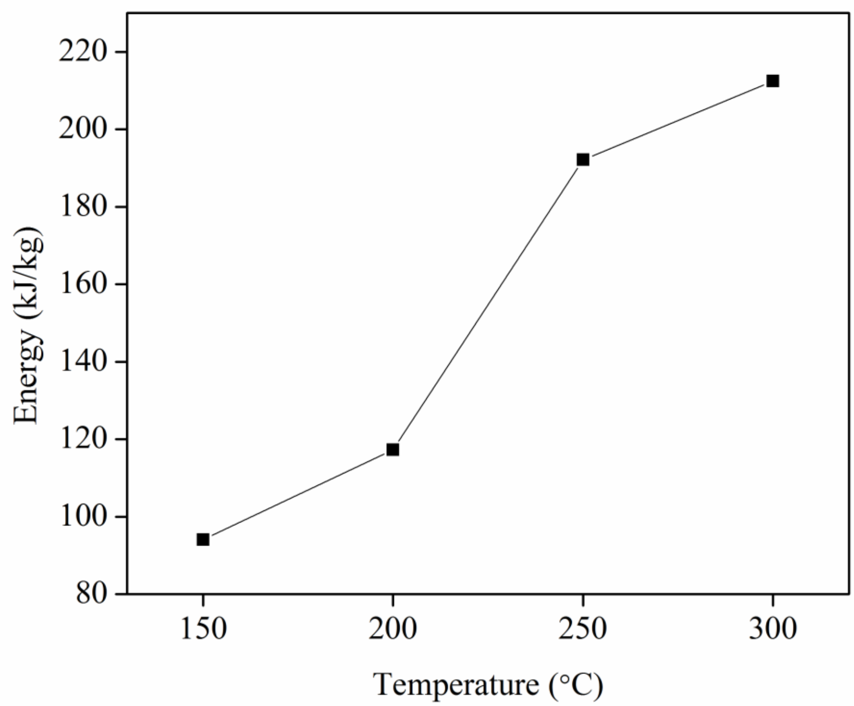

Figure 4.28: Energy required for hydrothermal treatment by recycling the wastewater

5. Chapter 5: Conclusion

The results of hydrothermal treatment of poplar coal in a batch autoclave reactor showed the significant amount of moisture from 26.85 to 5.02 wt % in coal can be removed. Ultimate analysis of coal revealed increasing of carbon percentage from 54.34 to 67.34 wt % and decreasing of oxygen content from 39.42 to 25.80 wt % during the hydrothermal treatment indicating loss of some oxygen functional group after hydrothermal treatment. Reducing the oxygen content reduces the self-ignition tendency of coal resulting in facilitating the transportation and storage of low rank coal [4]. During the hydrothermal treatment the hydrogen percentage of coal increases but the amount of the nitrogen and sulfur is almost the same. Decreasing the oxygen content and increasing the carbon percentage leads enhancing the heating value of the lignite coal from 27.57 to 29.90 Mj/Kg especially at high temperature where decreasing the oxygen is significant. Hydrophobicity of coal was analyzed by measuring the contact angle and reabsorption of moisture before and after treatment. Contact angle of coal increased from 27.8 to 96.4 degree by increasing the temperature especially treating at 300 °C which a sharp increase in contact angle was observed. The tendency of moisture reabsorption of coal was remarkably decreased after hydrothermal treatment due to reduction of oxygen functional group content, shrinking of the pore structure and coating the surface by tar [3, 8]. Increasing the hydrophobicity of the coal enhances the slurry ability [4] of the coal and reduces the expenses for preventing the moisture absorption after treatment. Analysis of liquor after filtration showed the leaching of some organic and alkali metals.

Liberated organics can coat the surface and prevent absorbing moisture [3]. Liberation of some alkali metals decreases the amount of ash in hydro-treated coal, in addition decreases the possibility of ash fouling in boilers [8, 17]. Ash analyzing shows the reduction in some alkali metals such as Mg (5.03 to 4.11 wt %), Ca (13.50 to 9.73 wt %), and some elements such as S (6.12 to 4.21 wt %) and Fe (5.03 to 4.98 wt %). Visual inspection of the surface of raw and treated coal by SEM shows the collapsing of the pores structure.

Due to long process time of the hydrothermal treatment negligible changes in properties of coal were observed after treatment by changing the size fraction of lignite coal. The results of the moisture, ash of the coal confirm this idea. Analysis for determining the best residence time for hydrothermal process showed that majority of the process takes place in the first 15 minutes. After that the rate of the reduction of the moisture and oxygen and rate of the increasing of the carbon percentage decreases noticeably. Increasing the initial pressure from 0 bar 20 bar can decrease the reaching time from 66 to 50.5 min at 200 °C and 97 to 73 min at 250 °C which causes reducing the energy required for hydrothermal treatment. In addition to that, the yield of the product increases from 58.5 to 64.53 % which shows the loss of the volatile decreases during the process. But the results show the moisture content of the coal increases from 5.96 to 8.08 wt % at 250 °C by increasing the initial pressure. Considering all the results for the moisture, yield and reaching time it can be concluded that the best initial pressure can be 10 bar where it causes a high reduction in the ramping time and minimum loss of volatile.

The results presented in this thesis shows the lignite coal can be prompted to a more valued coal during the hydrothermal treatment. By increasing demand for energy and increasing the cost of the high rank coal and other fuels such as gas and oil, hydro-treated coal can be a good replacement for them.

6. Chapter 6: Contributions to the Original Knowledge

It has been proved through our investigation that hydrothermal process is an efficient method for the moisture removal from low rank coal. It was also observed that some mineral matters leached out during the hydrothermal treatment, however this process is not an efficient way for separating mineral matter from low rank coal.

The proposed mechanism of the hydrothermal treatment was investigated and was proved by different analytical method during the study. Oxygen functional groups such as hydroxyl and carboxyl groups were removed from the organic components present in the coal by cleaving the loosely bounded hydrogen bonds and covalent bonds [9, 52]. These cause producing of CO_2 and CO gases during the process. As a result of that the generated gases like CO_2 push the moisture out from the pores to the liquid phase [11]. Meanwhile the destruction of the pores [8] limits the moisture reabsorption of the coal and makes the coal more hydrophobic resulting in less tendency of coal to reabsorb the moisture. Air drying after the hydrothermal process plays an important role for drying the coal. During the hydrothermal treatment inherent moisture of coal migrates to the surface of the coal, which can be easily removed by air drying at ambient temperature utilizing a minimum air flow rate of 5 L/min.

Moisture reabsorption of low rank coal after drying is a major issue in storage and transportation of the coal. It was proved through our experimental results that hydrothermal treatment especially at high temperature (250 and 300 °C) decreases the reabsorption ability thus there is no need to build the drying and power generation plant next to each other. In addition hydrothermally treated and dried coal can be easily transportable and export to the other countries.

Optimum condition for hydrothermal treatment process was also investigated to obtain the most value added coal utilizing minimum energy. Even though the process at 300 °C can remove more moisture from coal but the energy that has to be consumed is much higher in comparison with 250 °C and coal loses more volatile at 300 °C, thus treatment temperature at 250 °C may be more favourable. Optimum residence time of the process can be 15 minutes, longer treatment has not significant effect on the moisture removal and coal elements. Increasing the initial pressure up to 10 bar helps to decrease the loss of volatile matter hence a higher yield of the product can be archived finally.

1. Chapter 7: Future Work

One of the main purposes of hydrothermal treatment is changing the low rank coal to a value added coal that is feasible for gasification process and will minimize the green-house gas emission [5]. Hydrothermal treatment changes low rank coal to a hydrophobic coal and thus increases the slurry ability [4]. Analyzing the slurry ability of hydro-treated after the process can show how much hydrothermal process is efficient in increasing the slurry ability.

Conducting hydrothermal treatment in a batch reactor is an expensive way in comparison with thermal drying process and long time required to reach the desired temperature, thus it is necessary to optimise the conditions for reaching the desired temperature with minimum ramping time. Finding a method to solve these obstacles seems essential.

Applying continuous flow system can be an alternative method for reducing the expenses and making the process more feasible for commercial scale. Applying a reactor with input and output and using water as heating medium can give us the opportunity to control the process better. In this method the liquor can be collected in different intervals of time and can be analyzed thoroughly. Also hot liquor can be recycled as the heating medium and avoid the wasting of energy. In addition this method can be combined with fluidized bed to increase the moisture removal capability and separating the mineral matters by using the air as cooling medium of hydrothermal process and using this hot air as the medium for fluidized bed dryer.

1. Chapter 8: References

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2. Chapter 9: Appendix

A 1: Moisture content of raw and hydro-treated coal (dry basis)

	Raw	150 °C	200 °C	250 °C	300 °C
Moisture (wt %)	26.85	13.57	7.66	5.41	5.02

A 2: Volatile matter content of raw and hydro-treated coal (dry basis)

	Raw	150 °C	200 °C	250 °C	300 °C
Volatile matter (wt %)	34.56	32.6	31.51	31.32	28.24

A 3: Ash content of raw and hydro-treated coal (dry basis)

	Raw	150 °C	200 °C	250 °C	300 °C
Ash (wt %)	40.51	37.12	37.94	38.8	40.81

A 4: Fixed carbon content of raw and hydro-treated coal (dry basis)

	Raw	150 °C	200 °C	250 °C	300 °C
Fixed carbon (wt %)	24.94	30.28	30.55	29.88	30.95

A 5: Higher heating value of raw and hydro-treated coal

	Raw	150 °C	200 °C	250 °C	300 °C
Heating value (Mj/Kg)	27.57	27.58	27.65	28.82	29.90

A 6: Air drying of the raw coal

Time	0	17 hr	18.4 hr	20.75 hr	21.25 hr
Moisture (wt %)	26.12	12.05	11.11	9.9	9.5
Time	24 hr	43.75 hr	46 hr	51.5 hr	
Moisture (wt %)	8.85	2.96	3.02	3.49	

A 7: Effect of the amount of the liquid on the moisture content

	50 ml	150 ml	250 ml
Moisture at 200 °C (wt %)	9.8	10.2	10.4
Moisture at 250 °C (wt %)	7.3	6.8	7.7

A 8: Effect of the amount of the liquid on the ash content (dry basis)

	50 ml	150 ml	250 ml
Ash at 200 °C (wt %)	24.13	23.81	24.37
Ash at 250 °C (wt %)	24.82	25.01	24.53

A 9: Effect of the amount of the liquid on the ultimate analysis of coal at 200 °C (daf basis)

	50 ml	150 ml	250 ml
N (wt %)	0.94	0.93	0.93
C (wt %)	67.63	67.87	67.65
H (wt %)	4.95	4.99	4.91
S (wt %)	1.81	1.38	1.48
O (wt %)	24.67	24.83	25.03

A 10: Effect of the amount of the liquid on the ultimate analysis of coal at 250 °C (daf basis)

	50 ml	150 ml	250 ml
N (wt %)	0.98	0.97	0.98
C (wt %)	69.74	69.52	70.23
H (wt %)	4.94	4.93	4.98
S (wt %)	1.83	1.84	1.55
O (wt %)	22.51	22.74	22.26

A 11: Contact angle of raw and hydro-treated coal

	Raw	150 °C	200 °C	250 °C	300 °C
Contact angle (θ degree)	27.8	62.1	64.1	70	96.4

A 12: Penetration time of the raw and hydro-treated

	Raw	150 °C	200 °C	250 °C	300 °C
Penetration (s)	6	7.601	8.4	9.6	40.4

A 13: Effect of hydrothermal treatment on moisture reabsorption of coal

	Raw (wt %)	150 °C (wt %)	200 °C (wt %)	250 °C (wt %)	300 °C (wt %)
0	26.85	13.57	7.66	5.41	5.02
1 hr	19.2	13.8	11.2	8.53	6.23
2 hr	19.3	15.2	12.13	9.73	6.54
3 hr	19.1	15.64	12.76	9.84	6.58
4 hr	19.4	16.01	12.9	9.78	6.51
5 hr	19	16.47	13.04	9.62	6.47
6 hr	19.1	17.1	13.32	9.69	6.53

A 14: Effect of Hydrothermal treatment on moisture reabsorption of coal (dried coal)

	Raw (wt %)	200 °C (wt %)	250 °C (wt %)	300 °C (wt %)
0 min	0	0	0	0
30 min	9.46612	8.99159	7.56608	5.48709
60 min	12.47045	11.43769	9.42321	6.69014
90 min	13.35697	12.15315	9.41338	6.71948
120 min	13.58353	12.42386	9.80643	6.59627
180 min	14.73601	12.64623	10.19947	6.64124
240 min	15.9673	12.84927	10.65147	7.06182
300 min	16.85855	13.28019	11.03469	7.79304
360 min	16.9866	13.33516	11.38147	7.57042

A 15: Effect of hydrothermal treatment on ash structure of coal

	Raw	300 °C
Mg (wt %)	5.03	4.11
Al (wt %)	24.41	25.72
S (wt %)	6.12	4.21
K (wt %)	1.36	1.47
Ca (wt %)	13.5	9.73
Cr (wt %)	0.04	0.04
Fe (wt %)	5.03	4.98
Sr (wt %)	0.2	0.16

A 16: Effect of hydrothermal treatment on liberation of alkali metals

	150 °C	200 °C	250 °C	300 °C
Li (wt %)	0.253	0.391	0.324	0.342
B (wt %)	14.3	14.9	15.3	18.5
Na (wt %)	27.9	28.8	32.1	51.1
Mg (wt %)	222	251	222	291
Al (wt %)	0.0171	0.163	2.39	0.398
K (wt %)	14.4	16.8	34.7	76.9
Ca (wt %)	261	272	300	551
Ti (wt %)	0.0284	0.0387	0.0679	0.0101
V (wt %)	0.00104	0.00116	0.00348	7.50E-04
Cr (wt %)	0.006	0.00697	0.0129	0.0256
Fe (wt %)	2.31	4.56	2.86	1.99
Mn (wt %)	0.441	0.313	0.173	0.183
Co (wt %)	9.90E-04	6.20E-04	3.20E-04	1.10E-04

A 17: Effect of size fraction on moisture content of coal

	SF < 0.5 mm (wt %)	0 < SF < 1mm (wt %)
Raw	26.85	26.97
200 °C	7.66	8.14
250 °C	5.41	5.8
300 °C	5.02	3.48

A 18: Effect of size fraction on ash content of coal

	SF < 0.5 mm (wt %)	0 < SF < 1 mm (wt %)
Raw	40.51	23.14
200 °C	37.94	20.16
250 °C	38.8	25.68
300 °C	40.81	25.63

A 19: Effect of residence time on the moisture content at 250 °C

	Moisture (wt %)
0 min	8.56
15 min	6.49
30 min	5.96

A 20: Effect of residence time on the ash content at 250 °C (dry basis)

	Ash (wt %)
0 min	34.46
15 min	34.39
30 min	35.01

A 21: Effect of initial pressure on reaching time

	0 bar (min)	10 bar (min)	20 bar (min)
Reaching Time at 200 °C	66	51	50.5
Reaching Time at 250 °C	97	75	73

A 22: Effect of initial pressure on moisture content

	0 bar	10 bar	20 bar
Moisture at 200 °C (wt %)	8.98	9.65	12.25
Moisture at 250 °C (wt %)	5.96	6.1	8.08

A 23: Effect of initial pressure on ash content (dry basis)

	0 bar	10 bar	20 bar
Ash at 200 °C (wt %)	34.44	34.46	34.83
Ash at 250 °C (wt %)	35.01	35.44	35.29

A 24: Effect of initial pressure on yield of the product

	0 bar	10 bar	20 bar
Yield at 200 °C (wt %)	66.94	74.38	76.1
Yield at 250 °C (wt %)	62.2	65.2	70.2

A 25: Effect of initial pressure on yield of the product (dry basis)

	0 bar	10 bar	20 bar
Yield at 200 °C (wt %)	60.93	67.17	66.77
Yield at 250 °C (wt %)	58.49	61.22	64.53

A 26: Reaching time to desire temperature

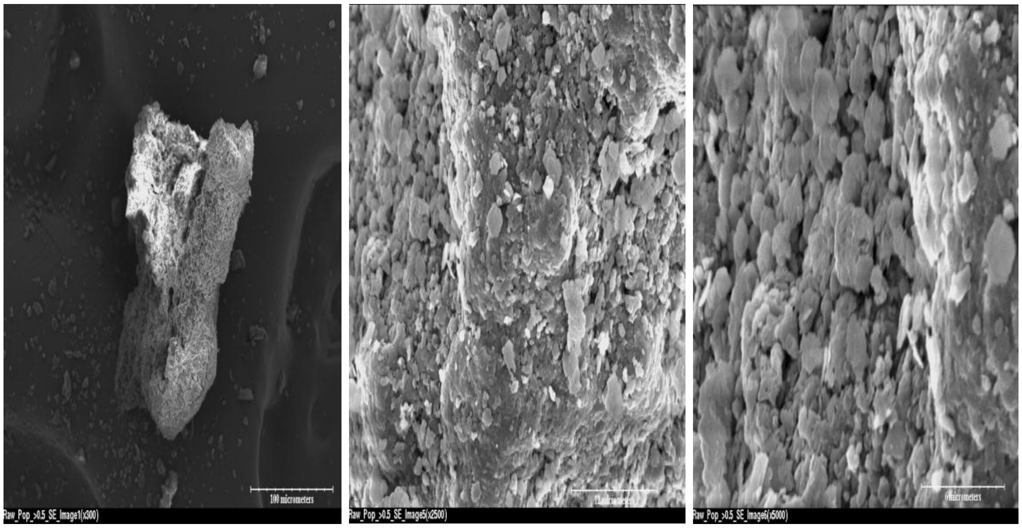
	150 °C	200 °C	250 °C	300 °C
Reaching time (min)	58	66	97	187

A 27: Reusing of the wastewater

	Fresh water	Reused water
Moisture at 200 °C (wt %)	8.98	11.72
Moisture at 250 °C (wt %)	5.96	7.31

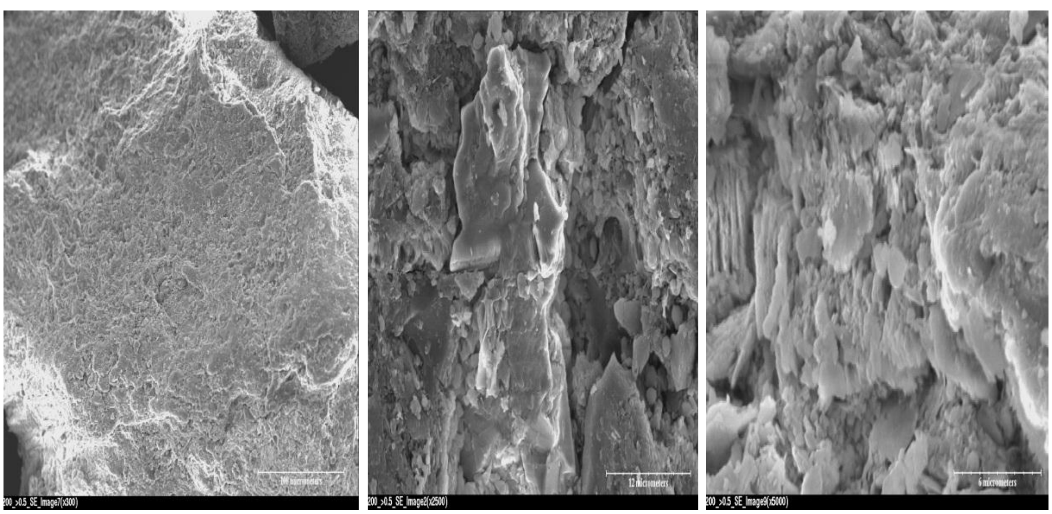
A 28: Effect of the hydrothermal treatment on the leaching of the organic carbon to the liquor

	Washed Coal	200 °C	250 °C	300 °C
TOC (mg/L)	21.1	139.9	580.8	1415



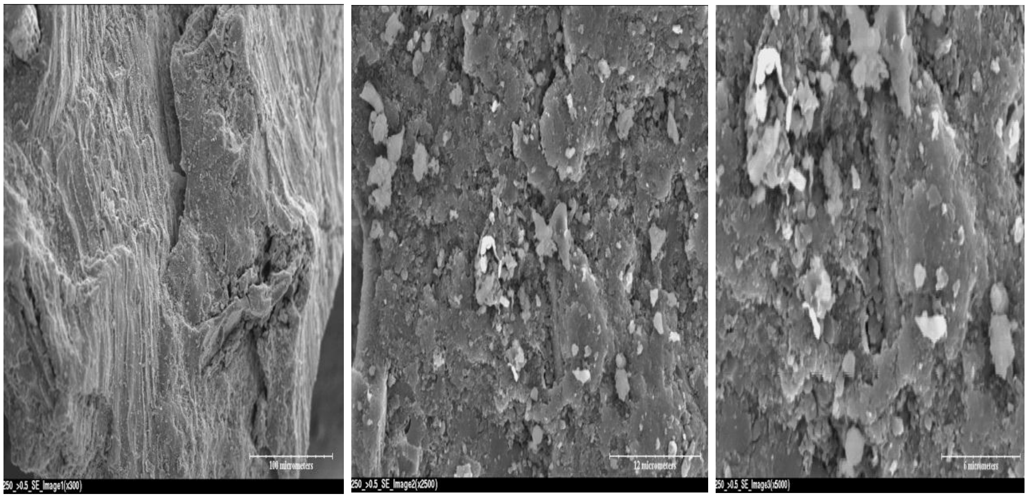
(a) (b) (c)

A 29: SEM analysis of raw coal, a: 300 x, b: 2500 x, c: 5000 x



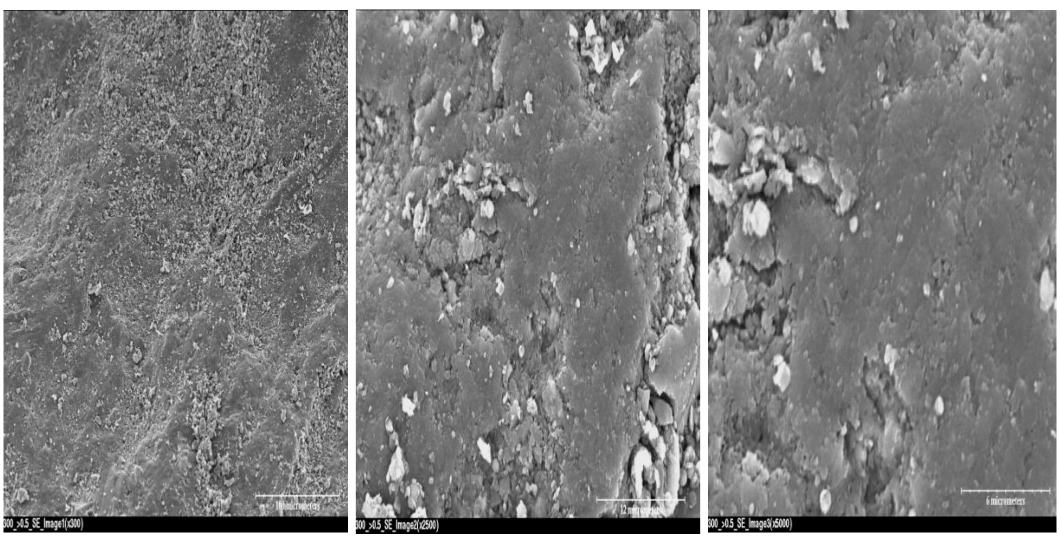
(a) (b) (c)

A 30: SEM analysis of hydro-treated cola at 200 °C, a: 300 x, b: 2500 x, c: 5000 x



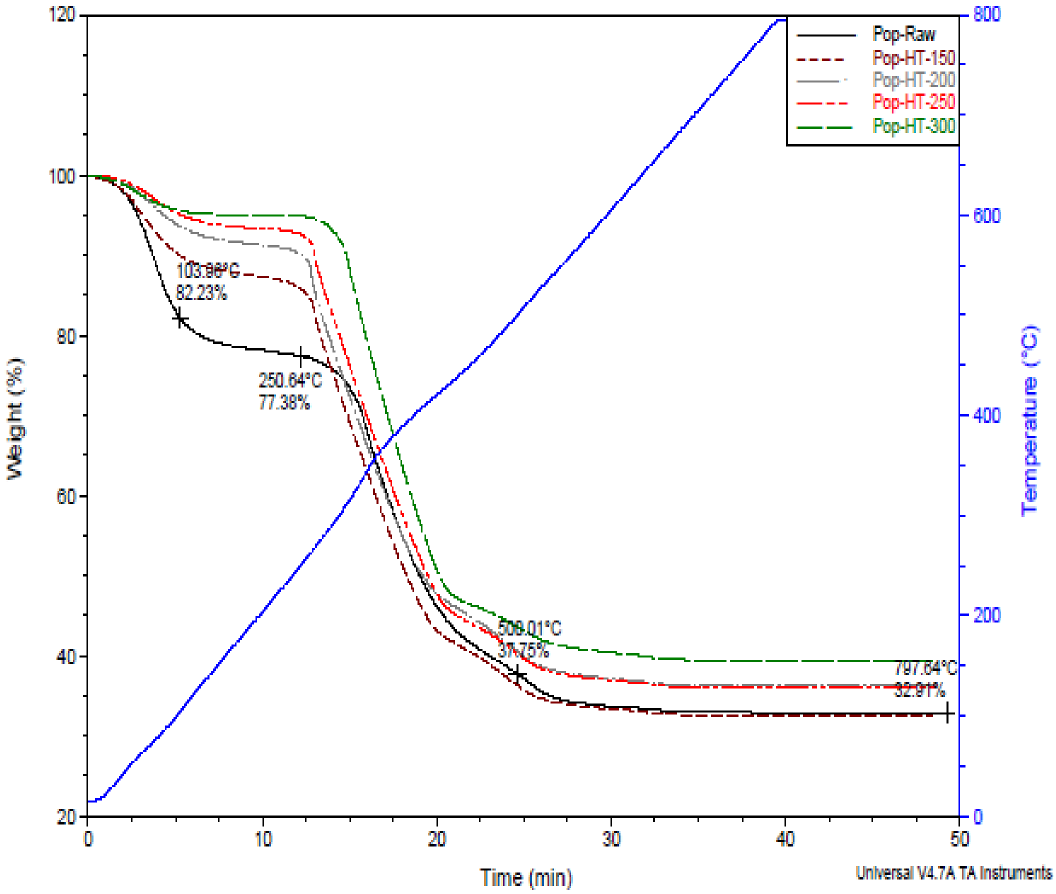
(a) **(b)** **(c)**

A 31: SEM analysis of hydro-treated cola at 250 °C, a: 300 x, b: 2500 x, c: 5000 x



(a) **(b)** **(c)**

A 32: SEM analysis of hydro-treated cola at 300 °C, a: 300 x, b: 2500 x, c: 5000 x



A 33: TGA analysis of raw and hydro-treated coal

A 34: Weight loss of the raw and hydro-treated coal during by TGA

	RT - 105 °C (wt %)	105 - 250 °C (wt %)	250 - 500 °C (wt %)	500 - 800 °C (wt %)
Raw	17.89	4.73	39.61	4.86
150 °C	8.33	4.9	48.93	5.38
200 °C	5.38	3.86	49.02	5.55
250 °C	4.1	2.88	51.73	5.31
300 °C	3.8	1.17	50.45	5.27

Parameter of the calculation is defined in Table A 36

A 35: Parameters of calculations

Parameter	Description	Value	Unit
h	Heat transfer coefficient	2.71	$\frac{w}{m^2 °C}$
A	Surface area of reactor	0.05966	m^2
C_p	Specific heat capacity of coal	1.6	$\frac{kJ}{kg°C}$
$C_{p\ (dried\ coal)}$	Specific heat capacity of dried coal	1.3	$\frac{kJ}{kg°C}$
m_{coal}	Weigh of coal	0.05	g
$m_{moistre}$	Weigh of moisture	0.013	g
T_∞	Ambient temperature	20	°C
h_v	Heat of evaporation	2260	$\frac{kJ}{kg}$

Calculation of energy required for hydrothermal treatment was divided into 3 steps:

1) Energy required for raising the temperature from room temperature (20 °C) to 250 °C (Calculated by Hysys)

$Q_1 = 172.16\ kJ$

2) Heat loss during raising temperature from room temperature (20 °C) to 250 °C

$$\frac{dQ_2}{dt} = hA\ (T\ -\ T_\infty) \rightarrow Q_2 = \int_0^{5820} hA(T - T_\infty)dt$$

We assume that the temperature of the reactor wall is the same as slurry and changing the temperature by time is linear.

$T = 0.0395t + T_\infty$

$$Q_2 = 0.0395hA\int_0^{5820} tdt = 108.16\ kJ$$

3) Heat loss during the 30 minutes of residence time

$$Q_3 = hA(T - T_\infty)\Delta t \ \rightarrow\ Q_3 = 66.93\ kJ$$

Total energy required for the process:

$$Q_{total} = Q_1 + Q_2 + Q_3 = 347.25\ kJ$$

Calculation of energy required for thermal drying was divided into 5 steps:

1) Energy required for raising the temperature from room temperature (20 °C) to 105 °C

$$Q_1 = m_{coal}c_p\Delta T = 6.8\ kJ$$

2) Energy required for removing moisture from coal (26 wt % of coal is moisture)

$$Q_2 = m_{moisture}h_v = 29.38kJ$$

3) Energy required for raising the temperature from 105 to 250 °C

$$Q_3 = (m_{coal} - m_{moisture})C_{p\ (dried\ coal)}\Delta T = 6.9745\ kJ$$

4) Heat loss during the removing moisture

$$Q_4 = hA(T - T_\infty)\Delta t = 49.473\ kJ$$

5) Heat loss during the raising temperature from room temperature to 250 °C

$$\frac{dQ_5}{dt} = hA\ (T - T_\infty) \rightarrow Q_5 = \int_0^{5820} hA(T - T_\infty)dt = 0.0395hA\int_0^{5820} tdt = 108.16\ kJ$$

Total energy required for the process:

$$Q_{total} = Q_1 + Q_2 + Q_3 + Q_4 + Q_5 = 200.7875\ kJ$$

Calculation of energy required for hydrothermal treatment with recycling the wastewater at 200 °C was divided into 3 steps:

1) Energy required for raising the temperature from 200 to 250 °C (Calculated by Hysys)

$Q_1 = 40.36\ kJ$

2) Heat loss during raising temperature from room temperature 200 to 250 °C

$$\frac{dQ_2}{dt} = hA\ (T\ -\ T_\infty) \rightarrow Q_2 = \int_{2760}^{5820} hA(T - T_\infty)dt$$

$$T = 0.0395t + T_\infty$$

$$Q_2 =\ 0.0395hA \int_{2760}^{5820} tdt = 83.83\ kJ$$

3) Heat loss during the 30 minutes residence time

$$Q_3 = hA(T -\ T_\infty)\Delta t\ \rightarrow\ Q_3 = 66.93\ kJ$$

Total energy required for the process:

$$Q_{total} =\ Q_1 +\ Q_2 +\ Q_3 = 191.12\ kJ$$