

STUDY OF BIO-OIL PRODUCTION FROM SEWAGE SLUDGE OF A MUNICIPAL WASTEWATER TREATMENT PLANT BY USING HYDROTHERMAL LIQUEFACTION (HTL)

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To overcome the problem of rapid depletion of natural energy reserves and consequent pollution caused by them, this work explored the possibility of utilizing sewage sludge biomass to produce bio-oil using hydrothermal liquefaction (HTL) pathway. In this study, effect of different reaction parameters such as reaction temperature, residence time, and sludge-to-water (ss-to-water) ratio on solid biomass conversion and bio-yield and its higher heating value (HHV) were investigated. Although maximum conversion of (99.7 %) and highest bio-oil yield (22.01 wt%) was achieved at 330 °C, however optimum temperature was chosen as 300 °C which produced conversion efficiency and yield of bio-oil very close (98.07 % and 21.5 wt% respectively) to what was obtained at 330 °C as lower temperature is beneficial for overall economy of the process. Similarly, a residence time of 60 min and ss-to-water ratio of 1:6 was screened to be producing optimized yield of bio-oil. HHV of different fractions bio-oil was much improved (30.18 MJ kg⁻¹ of acetone phase and 38.04 MJ kg⁻¹ of DCM phase) as compared to that of raw feedstock (12.74 MJ kg⁻¹). Carbon balance performed on the products indicated that maximum amount of carbon went to bio-oil phase (53.4 wt%). However, a significant portion of carbon was lost (33.9 wt%) due to the limitation of experiments at lab scale which involves evaporation and drying to reach final products. FTIR spectral analysis of different bio-oil phases showed that it was mainly made up of alcohols, alkane, ketones, aldehydes and carboxylic acids.

Keywords: *Hydrothermal Liquefaction (HTL), Sewage Sludge (SS), Bio-oil, Water soluble oil (WSO), Biochar, Higher heating value (HHV)*

1. Introduction

Extensive use of natural reserves of fossil fuels results into not only rapid depletion of these resources but also causes day-by-day increase in environmental pollution. At the same time, massive increase in population, urbanization and industrialization also result in increase in energy demand [1]. As estimated, population of world, by 2050, will be 9 billion and almost 99% of this increase is

expected to be coming from developing countries [2]. This rapid growth in population implies a multifold increase in energy consumption in these areas and hence the quest to find alternative sources of energy is even more pressing in future. These alternatives must not only be abundant in terms of sustainability but also renewable (having positive effects on the environment). In this context, waste biomass seems to be promising raw material for energy production as the utilization of waste biomass serves the two-pronged strategy of producing alternative energy on one side and on the other hand, efficiently handling the waste material which is anticipated to rise with population growth.

Sewage sludge, a waste biomass, poses serious threats to environment if not handled properly. For example, considerable amounts of chemicals including sulfur, chlorine, nitrogen, heavy metals present in sewage sludge may cause eutrophication [3]. Human sewage, owing to high organic content, is one of the main reasons for pathogenic bacteria and viruses in seawater which disturb aquatic life and ultimately impact human health when these infected seafood is consumed by humans [4]. Sewage sludge contains high amounts of organics (including carbohydrates, lipids, proteins etc.) and is an ideal feedstock to be used for biofuel production [5]. It is a biomass which is obtained as a waste from wastewater treatment plant and contains a high percentage of moisture content. Urbanization, mass migration and exponential growth in housing sector causing a continuous increase in sludge production [6], and hence its effective utilization is inevitable.

In Pakistan, open fields are used for rural waste and sewerage system is utilized for disposal of urban excreta, whereas the remaining waste deposited along roadside, into water-ways, or deposited as solid waste [7]. There are many environmental problems associated with these practices such as bad odor, production of secondary pollutants i.e. dioxins during incineration or burning of waste etc. These evil practices further add to the existing environmental problems connected with this sludge and hence increase problem severity.

Production of fuels from this waste biomass as a potential replacement of conventional fossil fuels would not only be a low-cost alternative but also renders an environmentally friendly as well as effective utilization of this waste [8]. Direct combustion and similarly pyrolysis are not the options for such a biomass because of its very high moisture content. However, a thermal conversion process of biomass into energy dense product in aqueous media, known as hydrothermal conversion process, has been the subject of many studies on sewage sludge [9].

Supercritical water gasification reaction, being on commercial scale, does not create products in liquid state or solid state and hence the existing infrastructure for solid and liquid fuel utilization cannot be used [10]. Hydrothermal liquefaction (HTL) of sewage sludge produces a range of products in different phases with a focus to produce liquid product. However, large quantities of solid (consisting of bio-coke and ash) and gaseous products are also produced hence giving a variety of products.

Although there has been number of studies performed on HTL of sewage sludge in different parts of the world, as mentioned above, yet the composition of sewage sludge varies around the world depending upon the eating and living habits of inhabitant [11]. There is not a single study on the sewage sludge liquefaction in Pakistan, as per author's knowledge, which demands not only thorough investigation of the sewage sludge produced in Pakistan, but also the understanding of its subsequent liquefaction behavior.

Current study focuses on utilization of sludge obtained from a local municipal sewage treatment plant in Pakistan. After comprehensive analysis of raw sewage sludge feedstock, HTL was performed with varying conditions of temperature, residence time, and biomass-to-solvent ratio in sub-critical

regime of water. Conversion of raw sewage sludge and liquid product selectivity was better than most of the studies performed at similar conditions of variable parameters [5]. Liquid products were characterized using proximate analysis, elemental analyzer, Fourier Transform Infrared Spectroscopy (FTIR), and Total Organic Carbon (TOC) analyzer. Carbon balance was also reported to show the total carbon lost during the liquefaction process as volatiles. Hence, this study serves as a foundation for future studies on HTL of sewage sludge produced in Pakistan.

2. Materials and Methods

2.1 Collection and preparation

The raw sewage sludge sample in wet form was collected from a local municipal sewage treatment plant (from the wastewater treatment plant of Bahria Town, Rawalpindi, a city in Pakistan). Raw sewage sludge (having 78% moisture) was dried in sunlight in open trays by covering them with a thin cloth to avoid dust accumulation. Dried sewage sludge was stored in sealed polythene bags for further use.

2.2 Characterization of sewage sludge

Moisture content of sludge sample was measured by using ASTM E871 method, ash content using ASTM E1755-01, volatile matter using ASTM E-872 and fixed carbon is the resultant of the summation of percentage moisture, ash, and volatile matter subtracted from 100. Ultimate analysis of raw sewage sludge sample was performed using CHNS analyzer (FLASH 2000 CHNS/O Analyzer by ThermoFisher Scientific) and based on the elemental analysis, higher heating value (HHV) which was calculated using DIN 51900 standard. The results of proximate and ultimate analysis of sewage sludge sample are shown in Table 1:

Table 1. Proximate and ultimate analysis and HHV of raw sewage sludge sample.

Proximate Analysis (wt%)					
Moisture		Ash		VM	FC
8.82		40.91		43.18	7.8
Ultimate Analysis (wt%)					HHV (MJ kg ⁻¹)
C	H	N	S	O	12.74
31.09	4.8	13.94	0.74	49.41	

2.3 Hydrothermal Liquefaction process

Dried sewage sludge sample (as per standard mentioned above) was put into a mini bench top reactor (4560 Parr Instrument Company) to perform HTL experiments batch wise. Schematic depiction of the experimental procedure is shown in Fig. 1. The main parts of HTL system includes reactor vessel with volume 1 L, stirrer, pressure and temperature gauges. In a typical experimental run, measured amount of distilled water and dried sludge was loaded into reactor. Reactor was sealed and purged with N₂ after loading and pressurized with N₂ to 1.0 MPa so that the residual air inside reactor is removed. The experiments were performed at different reaction temperatures (270 °C, 300 °C and 330 °C) for different sludge to moisture content ratios (1:2, 1:4 and 1:6) and for three different residence times (30 min, 60 min and 120 min). As the temperature was raised, pressure of the reactor increased due to vapor

pressure of solvent as well as thermal breakdown of larger molecules of feedstock to smaller units. After the desired residence time at set temperature, heating was stopped, the reactor was quenched with cold bucket of water (to bring temperature to about 100 °C) and then left to cool down to room temperature (about 45 min). It is important to mention that the heating and cooling time of the reactor was not included in the residence time. After cooling of the reactor, gases were vented before opening the autoclave.

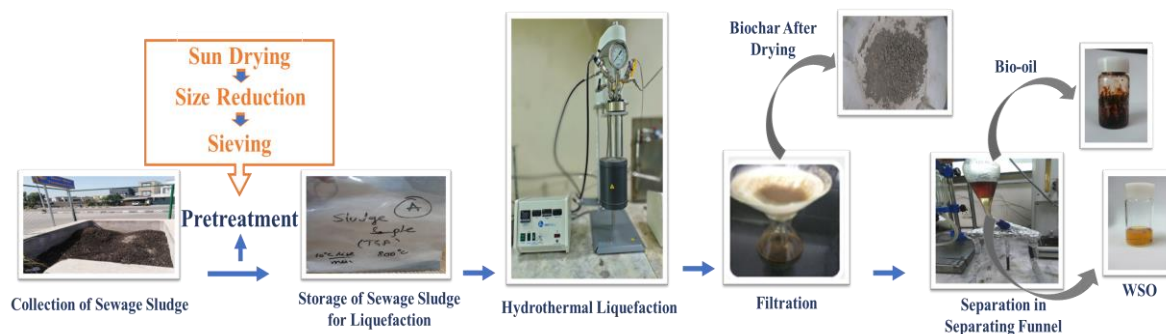


Figure 1. Schematic diagram of experimentation stage showing step by step procedure adopted for this study.

2.4 Products separation and characterization

After venting the reactor, it was opened, and the mixture of solid and liquid products was separated using Whatman No. 41 filter paper. The solid cake left on the filter paper was rinsed with acetone to separate organic phase present in solid residue and dried in the drying oven at 105 °C till constant weight. Filtrate was taken to separating flask so that organic oil phase is separated from aqueous phase having water-soluble oil (WSO) dissolved in it. The two phases are separated using liquid-liquid extraction. The reactor was rinsed using dichloromethane (DCM) and residual products (liquid and solid) was added to separating flask. To have a maximum separation and to standardize the process, a time of 1 h was provided before the phases were collected separately. Top layer consisting of aqueous phase with water-soluble oil (WSO) in it was dried in drying oven at 105 °C till constant weight and the bottom layer having organic fractions dissolved in DCM was dried at 70 °C. Residual mixture of oil which adhered to the components of reaction was finally washed with acetone and mixed with the organic fraction for maximum recovery of biocrude.

Conversion of the solid sewage sludge into liquid and solid products and overall losses were measured using following equations:

$$\text{Yield of bio-oil/WSO (wt. \%)} = \frac{\text{Mass of daf bio oil/WSO}}{\text{Mass of daf sewage sludge}} \times 100 \quad (1)$$

$$\text{Yield of biochar (wt. \%)} = \frac{\text{Mass of daf solid residue}}{\text{Mass of daf sewage sludge}} \times 100 \quad (2)$$

$$\text{Losses (wt. \%)} = 100 - (\text{sum of yields of bio-oil, WSO and solid residue}) \quad (3)$$

Bio-oil and WSO were analyzed in elemental analyzer as mentioned above, and HHV of the respective phases were calculated using DIN 51900 standard. Carbon content measured via elemental analyzer was used for carbon balance. Chemical functionalities of the products

and raw sewage sludge were obtained using a Perkin Elmer Spectrum Fourier transform infrared (FTIR) spectrometer with a resolution of 4 cm^{-1} in the range of $4000\text{--}400\text{ cm}^{-1}$.

3. Results and Discussion

3.1 Effect of Different Reaction Parameters

3.1.1 Effect of reaction temperature

Most important parameter of HTL process is reaction temperature as it is critical parameter in controlling ionic properties of water which helps dissolving the biomass components. Ionic product of water increases with the increase in temperature and reaches its maximum value at $300\text{ }^{\circ}\text{C}$ [12] and this is one of the reasons for achieving high conversion at $300\text{ }^{\circ}\text{C}$ in many studies [13, 14].

The temperature values investigated in this study are $270\text{ }^{\circ}\text{C}$, $300\text{ }^{\circ}\text{C}$ and $330\text{ }^{\circ}\text{C}$, for fixed sludge-to-water ratio of 1:6 and a residence time of 60 min (these values of sludge-to-water ratio and residence time were reached after screening study). With the increase in reaction temperature from $270\text{ }^{\circ}\text{C}$ to $300\text{ }^{\circ}\text{C}$, yield of bio-oil increased from 17 wt% to 21.5 wt%. A further increase in temperature to $330\text{ }^{\circ}\text{C}$ has increased bio-oil yield marginally to 22.01 wt% as shown in Fig. 2.

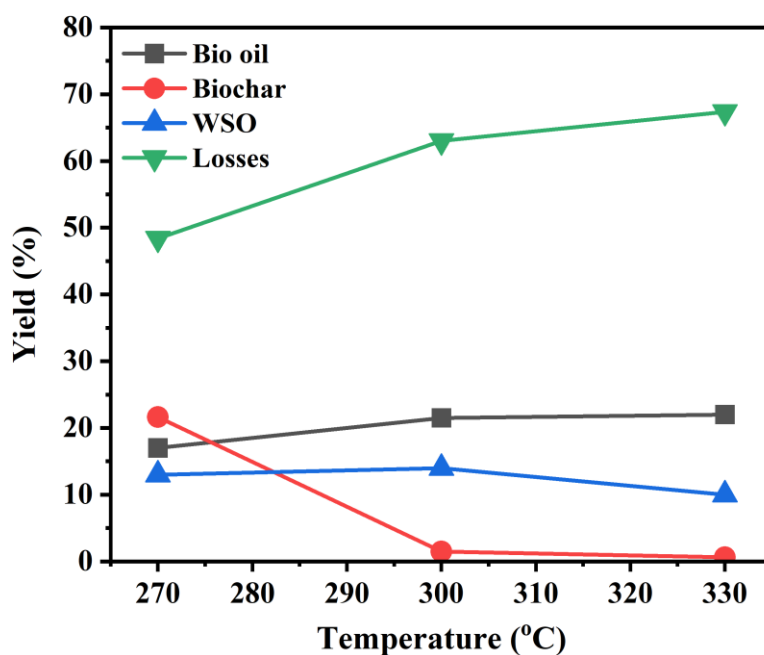


Figure 2. Effect of reaction temperature on yield of bio-oil, biochar, water soluble oil (WSO), and losses (reaction time: 60 min, sludge-to-water ratio: 1:6).

Conversion of the solid biomass also increased with temperature as evident by the decrease in biochar yield. From $270\text{ }^{\circ}\text{C}$ to $300\text{ }^{\circ}\text{C}$, yield of biochar significantly decreased from 21.61 wt% to 1.5 wt% and further increase in temperature decreased the biochar yield to 0.62 wt%. Effect of temperature on the conversion of solid biomass can be explained

considering the two observations. First is that the maximum conversion in this study, like the previous studies [Ref], is obtained at 300 °C which emphasizes on the ability of water to perform as an efficient solvent in dissolving solid biomass and reaction intermediates which promotes the liquid product yield. This dissolving power of water at high temperature is associated with the ionic product of water as discussed above. Second is that most of the organic part of the biomass had been converted to products at 300 °C as indicated by the very small amount of biochar yield. Further increase in temperature to 330 °C was not expected to improve bio-oil yield. However, it helped us improve our understanding of the reaction mechanism. For example, although the decrease in WSO yield from 14 wt% to 10 wt% and the decrease in yield of biochar from 1.5 wt% to 0.62 wt% was observed as the reaction temperature was increased from 300 °C to 330 °C, the yield of bio-oil however increased slightly from 21.5 wt% to 22.01 wt%. This was because the total losses during the reaction, which included gases and lighter fractions that could not be recovered during separation and drying process, increased from 63 wt% to 67.37 wt% as shown in Fig. 2. The ability of water to perform as a solvent at increased temperature is used to depolymerize larger molecules of solid biomass, as well as to dissolve the reaction intermediates which helps retarding the recombination reaction, has also been reported earlier [15].

3.1.2 Effect of reaction time

Previous studies on hydrothermal liquefaction exhibit that with increase in residence time, conversion of the feedstock initially increased and after certain increase of residence time conversion started decreasing. Initially biomass is dissolved in the solvent at high temperature and gets converted into bio-oil, biochar, gas, and reaction intermediates. As the reaction time is increased, lack of reactivity of solvent with reaction intermediates plays its part and repolymerization of the reaction intermediates forms biochar and hence a decrease in bio-oil yield. At the same time, some bio-oil components also get decomposed which results a decrease in bio-oil yield and an increase in gas yield [16, 17].

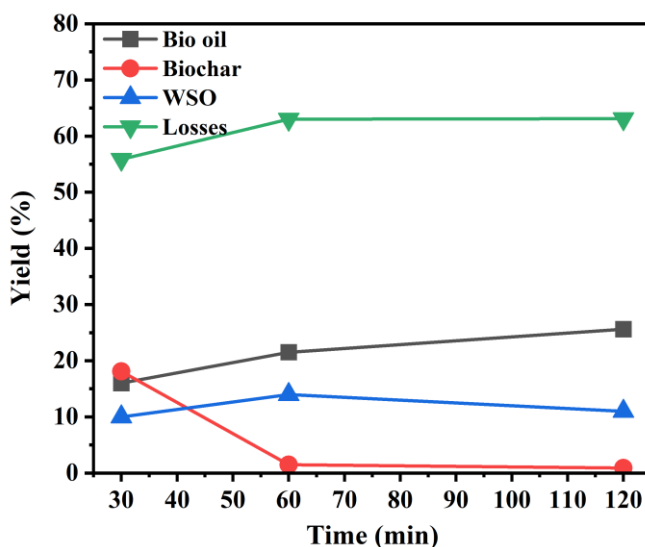


Figure 3. Effect of residence time on yield of bio-oil, biochar, water soluble oil (WSO), and losses (Temperature: 300 °C, sludge-to-water ratio: 1:6).

In this study, the effect of residence time was examined at a fixed temperature (300 °C) and sludge-to-water ratio (1:6). As the reaction time was increased from 30 min to 60 min, conversion of the biomass increased which was indicated by the increase in yield of bio-oil (16 wt% at 30 min to 21.5 wt% at 60 min) and that of decrease in yield of biochar (18.12 wt% at 30 min to 1.5 wt% at 60 min) as shown in Fig. 3.

However, with further increase of reaction time to 120 min, as opposed to previous studies where conversion decreased after a certain increase in reaction time, conversion did not decrease as yield of biochar remained constant (63.1 wt%) and yield of bio-oil increased (25.01 wt%). This shows that the repolymerization reaction, which causes the increase in biochar yield, was not significant even up to 120 min. Thus, the increase in bio-oil yield came from the decrease in WSO yield which was 14 wt% at 60 min and decreased to 11 wt% at 120 min reaction time. The highest yield for all reaction times was of losses which consisted of gas which was not quantified in this study as well as lighter compounds which evaporated during post liquefaction protocol including separation and drying. Losses also increased with the reaction time up to 60 min (from 55.88 wt% at 30 min to 63 wt% at 60 min) and then became stagnant as reaction time was increased to 120 min which indicates that the decomposition of raw material did not occur significantly after 60 min reaction time.

3.1.3 Effect of sludge-to-water ratio

The effect of sludge-to-water (ss-to-water) ratio on HTL products yield and conversion efficiency was investigated with fixed reaction temperature of 300 °C and reaction time of 60 min. As ss-to-water ratio was increased from 1:2 to 1:4 to 1:6, the conversion efficiency increased steadily as depicted by the decrease in biochar yield from 21.61 wt% (at 1:2) to 16.98 wt% (at 1:4) to 1.93 wt% (at 1:6) and yield of WSO phase remains almost unchanged. The yield of bio-oil increased respectively from 16 wt% to 16.5 wt% to 21.5 w%. Similar results have been reported by C Yang et al [15]. In HTL, ss-to-water ratio is one of the important parameters as it defines the concentration of solid in the media to be used as a solvent. As ss-to-water ratio was increased from 1:2 to 1:4 to 1:6, the amount of water increased and solid concentration decreased, which promoted solvolysis reaction leading to hydrolytic degradation of sewage sludge and thereby conversion efficiency increased. Since dissolution plays an important role to initiate subsequent degradation, at high solid concentration of sewage sludge, the relative interactions among fragments of reactants became less effective, thus reducing the dissolution of sewage sludge components [18].

The effect of ss-to-water ratio on yield of bio-oil, biochar, WSO, and losses during the reaction at temperature of 300 °C and at residence time of 60 min has been presented in Fig. 4.

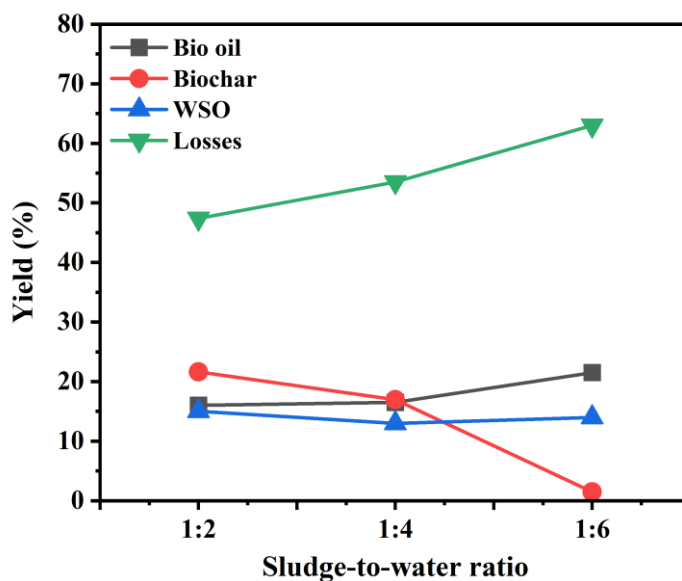


Figure 4. Effect of sludge-to-water ratio on yield of bio-oil, biochar, water soluble oil (WSO), and losses (Temperature: 300 °C, reaction time: 60 min).

3.2 Ultimate analysis and HHV

Ultimate analysis of the HTL products and subsequent HHV for reaction temperature of 300 °C, reaction time of 60 min and ss-to-water ratio of 1:6 has been presented in Table 2. HHV of the product bio-oil increased as compared to raw feedstock because of improvement in elemental composition.

Table 2. Ultimate analysis and HHV of raw feedstock, different phases on bio-oil and biochar (obtained at temperature: 300 °C, reaction time: 60 min, sludge-to-water ratio: 1:6)

Sample	Ultimate Analysis (wt%)					HHV (MJ kg ⁻¹)
	C	H	N	S	O	
Raw sewage sludge	31.09	4.80	13.94	0.74	49.41	12.74
Acetone Phase	60.79	8.41	11.99	0.51	18.30	30.18
DCM Phase	75.66	9.99	7.62	0.26	6.47	38.04
WSO Phase	24.12	6.83	10.28	1.85	56.92	12.12
Biochar	27.66	2.99	3.81	0.36	65.18	7.04

Carbon and hydrogen content of raw feedstock was low (31.09 wt% and 4.80 wt%) and oxygen content was high (49.41 wt%). However, carbon content of different bio-oil phases was higher (acetone phase 60.79 wt% and DCM phase 75.66 wt%) while that of WSO phase was lower (24.12 wt%) than raw feedstock (31.09 wt%). Similarly, oxygen content of acetone phase and DCM phase was low (18.30 wt% and 6.47 wt% respectively) while that of WSO phase was higher (56.92 wt%). The hydrogen content of all bio-oil phases was higher (acetone phase 8.41 wt%, DCM phase 9.99 wt% and WSO phase 6.83 wt%) as compared to that of raw feedstock (4.80 wt%). This increase in carbon and hydrogen content and decrease

in oxygen content affects the HHV a great deal as compared to nitrogen and sulfur content which do not impact HHV significantly as per DIN 51900 standard used for the calculation of HHV. Liquid-liquid extraction process employed in this study divided the bio-oil into oxygen rich WSO oil phase which created an affinity with water due to the presence of hydrogen bonding and the remaining bio-oil (DCM phase) had the lowest oxygen and hence highest carbon containing species and hence the highest HHV. The intermediate phase which was solubilized in acetone during rinsing of the reactor and other parts had intermediate amount of carbon and oxygen content and hence intermediate HHV. Carbon content of biochar is very low showing almost complete conversion of the organic part into different products. Very high oxygen content of biochar is a bit strange but that may be because the amount of oxygen has been calculated based on difference method.

3.3 Carbon Balance

To understand the distribution of carbon content into different products during HTL, determination of amount of carbon was performed on all three products (bio-oil, biochar and WSO) and carbon losses was calculated by subtracting the sum of all three product from the feedstock carbon content. Overall carbon balance for the optimized reaction conditions (reaction temperature of 300 °C, residence time of 60 min, and ss-to-water ratio of 1:6) has been presented in Fig. 5 which shows that the highest amount of carbon percentage (53.4 wt%) was found in bio-oil phase. This indicates that HTL of sewage sludge at the reaction conditions optimized in this study shows promising results. However, carbon content of the losses fraction was found to be significant (33.9 wt%) during this HTL reaction. Since the yield of losses fraction was huge (63 wt%), the carbon content of this fraction is not as big as it seems. Moreover, losses fraction is only found in laboratory experiments (in post liquefaction handling of the products including separation and drying), industrial scale HTL (because of the precise control and recycling of the solvents) is not expected to have such a high yield of losses fraction. The lowest percentage of carbon was found to be in biochar (1.5 wt%) which shows almost complete conversion of carbon from the sewage sludge to different products.

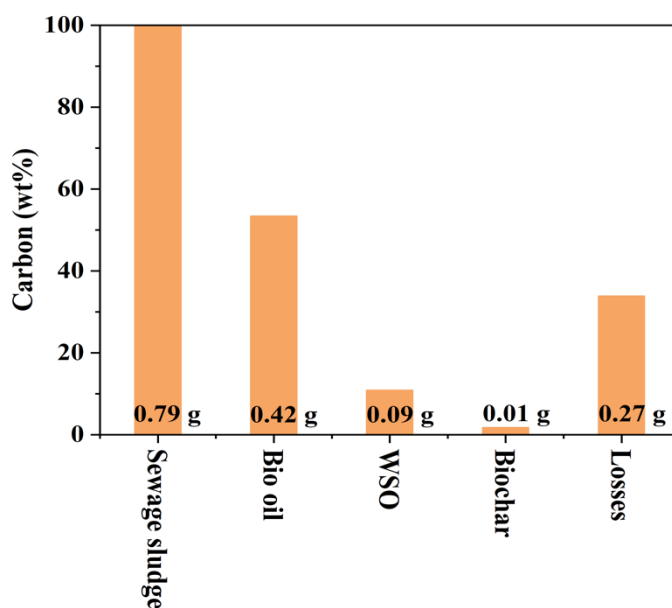


Figure 5. Distribution of carbon present in raw sewage sludge into bio-oil, water soluble oil (WSO), biochar, and losses (Temperature: 300 °C, reaction time: 60 min, sludge-to-water ratio: 1:6)

3.4 FTIR Analysis

Fig. 6 shows the FTIR spectra of the raw sewage sludge, bio-oil obtained via DCM rinsing as well as via acetone rinsing and the WSO phase produced at temperature of 300 °C, reaction time of 60 min and sludge-to-water ratio of 1:6. Raw sewage sludge showing the presence of many different types of functional groups where carbon is associated with hydrogen, with oxygen, with nitrogen, and with other carbon. Similarly other functional groups like -OH (1418 cm^{-1}), NO (1540 cm^{-1}), and S=O (1015 cm^{-1}) were also found indicating heterogenous nature of the raw feedstock. However, in different phases of bio-oil (DCM phase, acetone phase and WSO), nitrogen containing and sulfur containing species were not found which implies that these components might have ended up in biochar as reported earlier [19] or it might have been lost during separation process. The bands around $2840 - 2950\text{ cm}^{-1}$ in DCM and acetone phases correspond to the stretching vibration of alkyl C-H . However, the broad band at 3262 cm^{-1} in WSO phase represent stretching vibrations of -OH groups. This shows the segregation of the bio-oil into hydrophobic (DCM phase with the presence of C-H groups) and hydrophilic (aqueous phase with the presence of -OH groups) while separation was performed in separating funnel. The bands at 1635 and 1652 cm^{-1} were consistently found in raw feedstock and in all phases of bio-oil correspond to the stretching vibrations of C=C groups indicate the presence of C_6 rings [20]. The small peak at 1157 and 1097 cm^{-1} in DCM phase and at 1166 cm^{-1} in acetone phase can be assigned to C-O-C ether groups which was not observed in WSO [21,22].

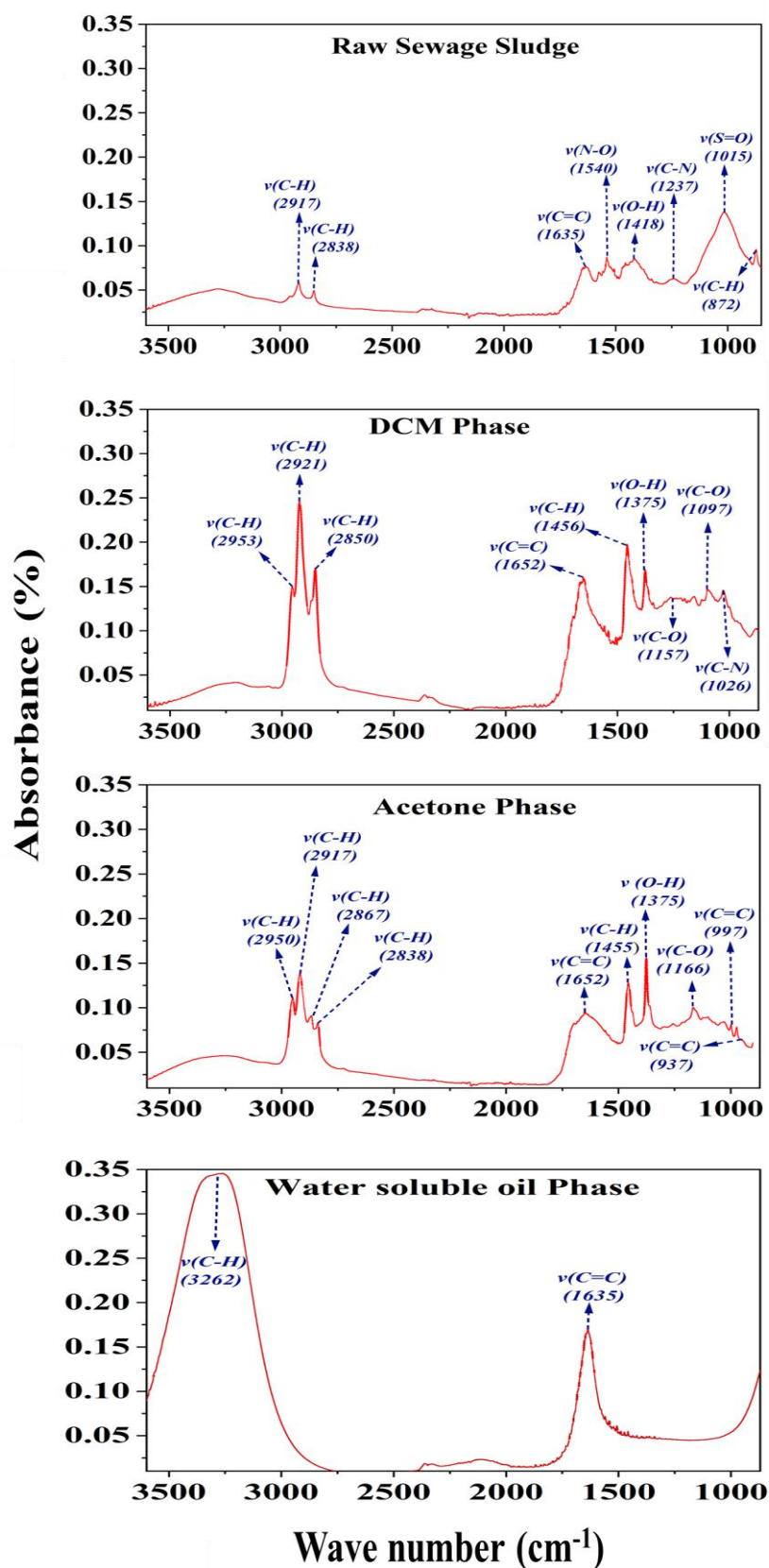


Figure 6. FTIR spectra of raw sewage sludge and different bio-oil fractions including DCM phase, acetone phase and WSO phase (obtained at temperature: 300 $^{\circ}\text{C}$, reaction time: 60 min, sludge-to-water ratio: 1:6)

4. Conclusions

This study emphasizes the utilization of sewage sludge as a potential biomass for biofuel production as it helps solving the issues of energy production using renewable feedstocks as well as efficient disposal of sewage sludge simultaneously. This work investigated the bio-oil production potential of sewage sludge as a waste biomass using HTL as a thermal conversion route. Sewage sludge in this work has been found to be a favorable feedstock for bio-oil production via HTL mainly because of its very high inherent moisture content. Through screening of different reaction parameters, reaction temperature of 300 °C, a residence time of 60 min and ss-to-water ratio of 1:6 produced high quality bio-oil in terms of its HHV with almost complete conversion (98.07 %) and high yield (21.5 wt%). Product separation process which included liquid-liquid extraction and drying of bio-oil increased the losses fraction up to 62.57 wt% having carbon content of 33.9 % of the original feedstock. Since this product separation protocol is not adopted at large scale production, these losses are not expected there.

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