Recovery of Cyclohexane from Oil Sands Gangue Using Microwave: Influence of Fine Particles

By

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Abstract

The extraction of bitumen from oil sands using non-aqueous extraction (NAE) techniques has the potential to replace currently used water-based extraction techniques. High bitumen recovery rates, lower freshwater requirements, and elimination of afterward tailing ponds are all advantages of non-aqueous extraction. Other benefits include a significant reduction in energy use and greenhouse gas emissions related to global warming and ozone depletion.

Using an organic solvent, bitumen is extracted from the oil sands ore during the nonaqueous extraction process, leaving behind a mixture of coarse and fine solids containing water, residual bitumen, and residual solvent (cyclohexane in this study), or “gangue”. Regardless of its numerous advantages, a significant environmental and economical drawback of the NAE method is the removal of solvent from the gangue post extraction.

A well-defined procedure to control the gangue composition was necessary in order to accurately analyze the impact of gangue components on solvent recovery from the gangue. Reconstituted gangue samples were prepared to create a synthetic sample whose drying behavior represented that of the non-aqueous extraction gangue. The utilization of reconstituted gangue was necessary because it represented samples whose composition could be precisely controlled for analysis.

This research demonstrated the effect of varying the content of fine particles at constant residual bitumen, water, and cyclohexane contents on the removal of cyclohexane from reconstituted gangue using two different solvent removal mechanisms: microwave-only in and air-drying followed by microwave. Heat was generated internally within the reconstituted gangue during the microwave experiment upon the interaction of the dipolar molecules with microwave radiation.

For reconstituted gangue samples undergoing only microwave heating, cyclohexane required more time to go through phase change, regardless of fine particles content. The temperature at which cyclohexane underwent phase change was significantly depressed for all samples undergoing microwave heating for all contents of fine particles. There was no apparent difference between the duration of cyclohexane evaporation in samples with 10% and 20% fine particles. The time required for cyclohexane to be removed from the gangue becomes independent of fine particles content at increased contents of fine particles. The maximum temperature reached by the Soxhlet solids remained unchanged for gangue samples with 10 wt.% fine particles but somewhat increased upon the addition of 20 wt.% fine particles, relative to samples containing 0 wt.% fine particles.

For reconstituted gangue samples undergoing air-drying prior to microwave heating, the duration at which cyclohexane underwent phase change reached its maximum at 10 wt.% fine particles content. This duration was similar for samples containing 0 wt.% and 20 wt.% fine particles. The temperature at which cyclohexane underwent phase change was comparable to cyclohexane's normal boiling point for all contents of fine particles. The duration of cyclohexane evaporation in reconstituted gangue samples containing 10% and 20% fine particles was doubled and tripled, respectively, relative to reconstituted gangue samples containing no fine particles. The time required for cyclohexane to evaporate from the reconstituted gangue significantly increases at increased contents of fine particles. The average maximum temperature reached by the Soxhlet solids was independent of the content of fine particles. Finally, fine particles accelerated the recovery of cyclohexane using microwave and lowered the evaporation onset temperature.

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1. Introduction

1.1. Background

The oil sands industry is a powerful source of Canadian energy that will continue to play a major role in Canada's economic growth in the upcoming decades. Oil sands are unconventional deposits located in various sites around the world, with Venezuela and Canada having the most important deposits in the Orinoco Oil Belt and Athabasca Oil Sands, respectively. Alberta's oil sands underline 142,000 km^2 of land and are mainly present in three areas: Athabasca, Cold Lake, and Peace River with Athabasca deposits being the largest of the three. After Saudi Arabia and Venezuela, the Athabasca Oil Sands in Alberta contain around 165 billion barrels of crude oil, making it the third-largest oil reserve in the world[1]. The accessibility and geologic locations of conventional and unconventional oil deposits differ; conventional oil deposits are frequently found in specific reservoirs and are typically simple to access, whereas unconventional oil deposits are found in pore spaces over a large area and thus require sophisticated extraction techniques.[2]

Oil sands are a mixture of sand, water, clay, and a heavy hydrocarbon called bitumen, which is the high molecular mass and viscous component of interest. Because of its viscosity, treatment by dilution or heating is necessary for bitumen to be pumped and therefore upgraded into gasoline and diesel fuel after extraction.

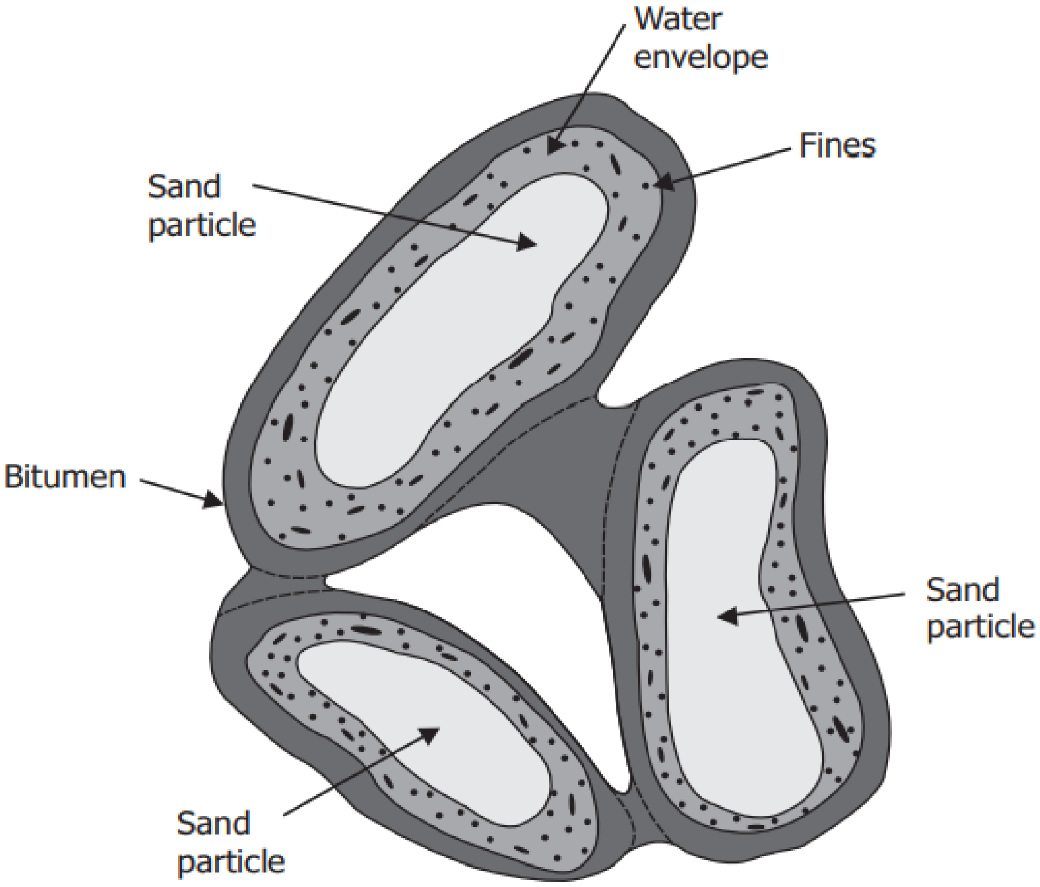

Figure 1. A schematic model structure of Athabasca oil sands.[3]

Alberta produced around 4 million barrels of bitumen per day in 2020[4] and $105 billion was provided to Canada's gross domestic product (GDP) in the same year[5]. The oil sands industry is predicted to contribute $1.7 trillion to the Canadian economy over the next 25 years. The future of energy in Canada will be secured by sustainably developing Canadian oil sands and expanding Canada's capacity to pursue more eco-friendly bitumen extraction methods.

1.2 Current Commercial Extraction Techniques

Unconventional oil requires advanced extraction techniques because of its viscosity and inability to flow on its own. Modern extraction techniques utilise two main extraction techniques to extract bitumen from oil sands depending on the depth of the oil sands deposits, such as surface mining and in situ techniques. Presently, surface mining methods account for ~47% of current production, with the remaining ~53% extraction via in situ methods.

1.2.1 Surface Mining

Surface mining is utilized when oil sands deposits lie within 70 metres of the earth surface. About 20% of oil sands deposits are accessible for surface mining. In this technique, vegetation is initially removed from the surface, and the oil sands deposits are shoveled into haul trucks and transported to crushers where large clumps are broken down. Afterwards, the bitumen-production process begins and consists of four significant steps:[6]

(i) Ore preparation, where hot water and caustic soda (NaOH) are added to the oil sands, producing a slurry which can easily be pumped to the main processing plant. The high-water temperature drops the viscosity of bitumen while the high pH alters the surface charge and interfacial tensions of bitumen and solids and prevents solids from sticking to the bitumen. The slurry, which consists of reduced-size lumps, is then fed into hydro-transport pipelines.

(ii) Hydro-transport pipeline, where the liberated bitumen droplets attach to air bubbles that were entrained during the ore preparation step. The slurry at the exit of the hydro-transport pipeline is diluted with water and fed into gravity separation vessels within the extraction plant.

(iii) Bitumen extraction, where bitumen is separated by gravity from the coarse solids by a water-based separation process, producing an intermediate bitumen froth product. The aim here is to recover the bitumen part and reject the heavy solids. Due to the previously added NaOH, bitumen is now able to liberate from solids' surface in the form of droplets. The liberated bitumen droplets either engulf or attach to air bubbles generated from forced aeration into the mixture and rise to the top of the vessel where they are collected as bitumen froth. The heavy solids sink to the bottom and are then pumped out to the tailings plant.

(iv) Froth treatment, since no further separation can happen by water-based gravity separation, either a naphthenic or paraffinic solvent is added to further reduce the bitumen viscosity and remove remaining water and solids. The rest of the mixture containing unrecovered bitumen, water, and solids is discharged to tailing ponds.[7]

The operations that take place between steps (i) and (iv) are standard, to a large extent, among many oil sands operators. Furthermore, oil sands pioneer, Dr. Karl Clark, was the first to experiment with aqueous extraction methods using hot water and a chemical agent in 1929[8]. The Clark hot water extraction method, abbreviated as CHWE, provided the basis for large-scale oil sands mining projects decades later and has been commercially utilized since 1967.[8]

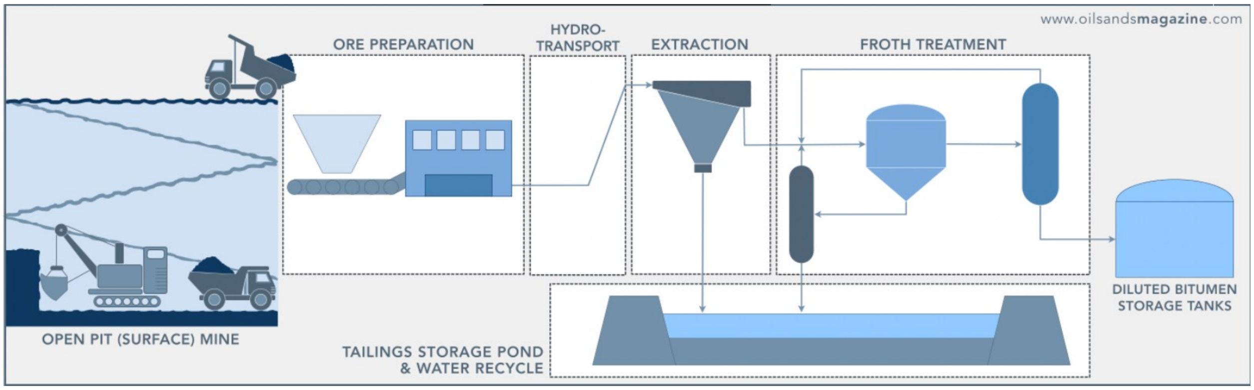

Figure 2. Process overview of surface mining extraction technique.[6]

1.2.2 In-situ Techniques

While mining activities can recover 20% of the Canadian oil deposits, the balance is recovered using in-situ techniques. In-situ technologies are utilized when oil sand deposits are located at least 75 meters below the surface.

One of the most common in-situ recovery techniques is steam assisted gravity drainage, abbreviated as SAGD. In this technique, two horizontal wells are drilled with one being slightly higher than the other. Steam is then injected into the top well, causing the bitumen to become fluid enough that it is able to flow into the second well[9]. The bitumen and steam emulsion is then pumped to the surface and transported for separation and further upgrading. Because the sand remains in the ground during the bitumen recovery process, tailings ponds are not generated. Nevertheless, this technique can only offer a maximum bitumen recovery of 60% and requires a large volume of steam to heat up the bitumen in the ground by burning natural gas, which generates greenhouse gas emissions.

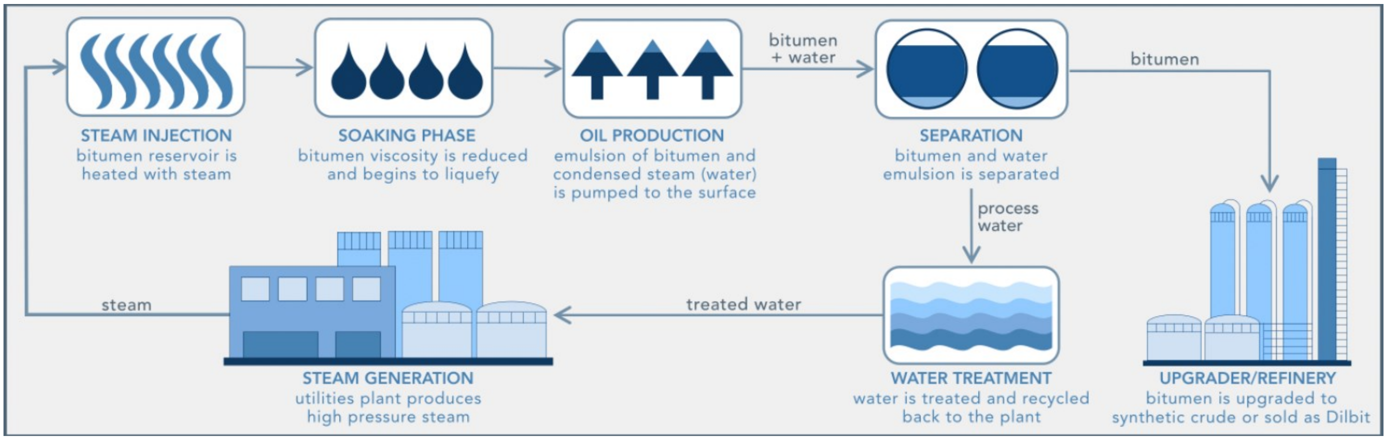

Figure 3. Process overview of SAGD extraction technique.[9]

The other common technique is cyclic steam stimulation, abbreviated as CSS. A single vertical well is drilled, and high-pressure steam is injected into the bitumen deposit. The steam is kept under high pressure to soak for multiple days to weeks, allowing the reservoir to become fully saturated and therefore reducing the viscosity of bitumen. The flow is then reversed, and the bitumen/steam mixture is pumped up the same well to the surface. In the in-situ techniques of SAGD and CSS, water is recovered and recycled back to the plant, producing no tailings ponds.[10]

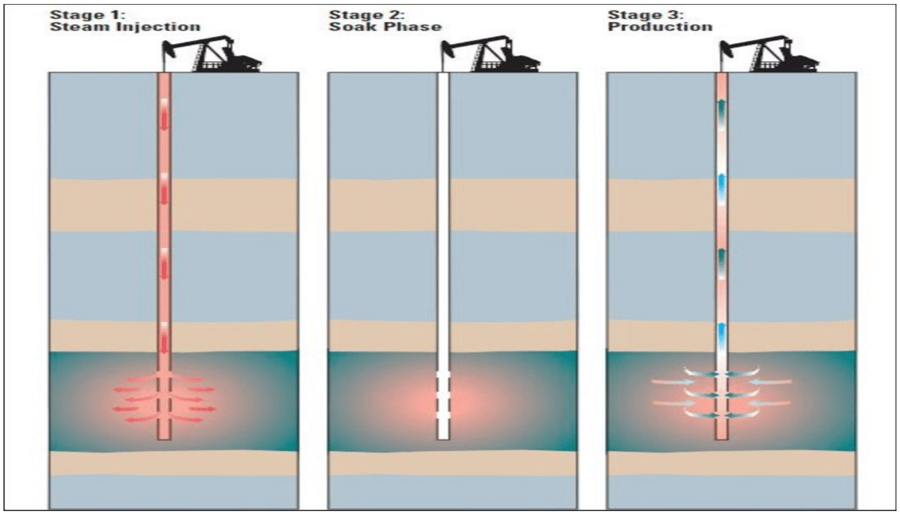

Figure 4. Overview of CSS extraction technique.[11]

While SAGD and CSS are the most utilised in-situ recovery techniques, there are other additional techniques to extract deep bitumen deposits; Toe-to-Heel Air Injection, where ignited air is used, and Vapour Extraction Process, where solvents are used. When compared to surface mining techniques, in-situ techniques have a smaller footprint, more efficient water utilisation, no tailings ponds, and lower construction, maintenance, and operation costs[9]. However, disadvantages of in-situ techniques include lower bitumen recovery rates, higher degrees of uncertainty, and elevated green house gas (GHG) emissions. Bitumen recovery rates of in-situ extraction techniques range from 40% to 60%, whereas the average surface mining bitumen recovery rates are 90% and can reach 95%.[9]

1.3 Disadvantages of Current Commercial Extraction Techniques

The aforementioned extraction techniques can have both environmental and economical drawbacks, including high green house gas emissions, high water consumption, energy intensity, accumulation of tailing ponds, and difficulty recovering bitumen from low grade and oil-wetted ores.

1.3.1 High Green House Gas Emissions

The oil and gas sector is Canada's fastest-growing source of greenhouse gas emissions[12]. The major emissions of concern are carbon dioxides, nitrogen oxides, and sulfur dioxides. GHG emissions are produced when hydrocarbons are combusted, trapping heat in the atmosphere, and causing temperatures to rise. These emissions also contribute to air pollution and rising ocean levels, creating extreme weather conditions[12]. Canada's global share of GHG emissions in 2018 was 1.5%, totaling 729 megatons of carbon dioxide[13]. Similarly, it is estimated that hot water extraction techniques produce 146 g of NOx and 30 g of SOx for every barrel of bitumen produced.

1.3.2 High Water Consumption and Energy Intensity

The amounts of water needed in current commercial extraction techniques differ depending on the technique utilised and can be in the form of steam or hot liquid water, most of which is drawn from the Athabasca River. In surface mining operations, 3 to 4 barrels of fresh water are used to produce one barrel of bitumen, while in-situ techniques use an average of 0.4 barrels of fresh water to produce one barrel of bitumen. In 2019, Suncor Energy alone consumed 11% more fresh water for its operations and had a total water consumption of 143 million cubic meters in the same year[14]. Furthermore, energy is required in surface mining to transport the ore, crush it, and heat the water used in the bitumen extraction step to separate bitumen from the oil sands ore. The increase in water consumption is directly proportional to the increase in energy consumption as more thermal energy will be required to heat the water for mining operations or produce steam for in-situ operations.

1.3.3 Accumulation of Tailings Ponds

Tailings ponds are man-made ponds that hold waste from the extraction and upgrading of oil sands. Water, sand, silt, clay, bitumen that has not been recovered, and other chemical toxins such as naphthenic acids, cyanide, arsenic, cadmium, chromium, copper, lead, and zinc make up their composition. The toxic materials present in the tailings ponds along with their enormous sizes make the management of these tailings one of the most complicated environmental issues facing the oil sands industry. Although mining operations recycle 75% of the water from tailings ponds back into the extraction process, tailings ponds are still growing[15]. The investment in tailings reduction technologies by oil sands operators is about $800 million[15]. For example, Suncor and Shell are examining mitigation technologies that can reduce the impact of tailings ponds, like Suncor's Tailings Reduction Operations (TRO™) and permanent aquatic storage structure (PASS), in addition to Shell's commercial-scale Atmospheric Fines Drying (AFD).

1.3.4 Low-grade and Oil-wetted Ores Issues

Bitumen recovery rates using current commercial extraction techniques can surpass 90% because of the ores' water-wettability, which allows bitumen to be separated from the sand grains[3]. However, water-wet low-grade ores, i.e., oil sand ores containing high amounts of fine particles (solids with particles with sizes <45 µm) and low bitumen contents, result in poor froth quality and recovery rates below 60%. This is because the higher fines content affects the ability of bitumen to attach to air bubbles and reduces froth quality, therefore decreasing bitumen recovery rates[3]. According to AER directive 082, if the average bitumen content of the ore is 11 wt.% or greater, the recovery rate should be at least 90 wt.%[16].

The cut-off percentages for high, medium, and low-grade ores according to the Alberta oil sands royalty guidelines are 13%, 10%, and 8% bitumen, respectively[17]. Eventually, the availability of high-grade oil sand ores will decrease, and companies will be directed to process more medium and low-grade ores in the future. In addition, current water-based extraction techniques are unfeasible for bitumen recovery from oil-wetted ores found in Utah and Indonesia and result in low recovery rates.

Current commercial extraction techniques hold air, water, and land impacts. It can be concluded that the root cause of the problems associated with current commercial extraction techniques is water usage. If industries continue to grow under current practices, more fresh water will be consumed resulting in the increase of energy use, more emissions of greenhouse gases, and more accumulation of tailings ponds. For this reason, an alternative extraction technique that eliminates water should be considered in order to overcome the disadvantages of water-based extraction techniques. Recently, interest in non-aqueous extraction (NAE) of bitumen from oil sands has increased as an alternative to the widely used water-based extraction techniques. All the existing problems with water-induced extraction could be solved with NAE.

1.4 Alternative Extraction Technique: Non-Aqueous Extraction

The use of solvents is an alternative method for recover bitumen from oil sands; non-aqueous extraction methods have the potential to significantly reduce water use, eliminate tailings ponds, increase energy efficiency, and reduce GHG emissions while maintaining high bitumen recovery rates. The concept of using solvents for extraction processes is not recent; discussions over NAE have started decades ago, but the extraction technique is yet to be implemented on a commercial scale. Furthermore, the increasing concerns over the environmental impacts of tailing ponds and water usage by current commercial extraction techniques have renewed interests towards NAE techniques. Figure 4 summarises the process of extracting bitumen from oil sands using an organic solvent.

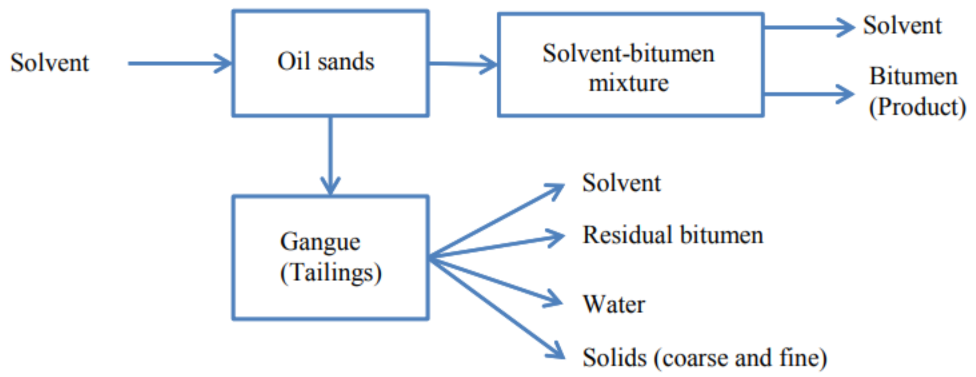

Figure 5. Flowchart of NAE extraction of bitumen using organic solvent.

To be considered as a feasible and competent replacement to current commercial extraction techniques, NAE must reduce water and energy consumption, maintain a high bitumen recovery rate at room temperature and ambient pressure, maximize solvent recovery from the gangue, and provide low fines in the final bitumen product. There are two technical barriers associated with NAE technique: 1) The presence of fine particles in the resulting bitumen-solvent product and 2) The solvent losses to the extraction gangue. The presence of fine particles reduces the value of the bitumen product and additional work will be required to remove the fines. Therefore, the finished bitumen product must have a low fines content in order to be used as refinery feed. At the end of the extraction process, NAE technique produces a waste material consisting of four main components: excess solvent, unrecovered/residual bitumen, water, and solids. Essentially all the water originally present in the oil sands ore is retained in the gangue during cyclohexane extraction. The solids component of the gangue consists of coarse and fine solids similar to the original oil sands ore. The solvent must be recovered from the extraction gangue for two critical reasons: environmental toxicity and cost of solvent.

The selection of a proper solvent for NAE plays a significant role in its implementation on a commercial scale. An optimal solvent should have high solubility of bitumen resulting in high recovery rates, minimize the transfer of fine solids to the final product, be easily removed and recovered from the extraction gangue, and have the least residual concentration[18].

Liu et al. conducted a study that showed how various solvents affect bitumen recovery. The study included alkanes, cycloalkanes, and toluene. They revealed that when cycloalkanes were taken as solvents, most of the heavy components (e.g., resins and asphaltenes) could be dissolved into the solvent. However, for alkanes, bitumen-heavy substances could not be easily extracted and therefore bitumen recovery was low. Toluene, on the other hand, showed a relatively high bitumen recovery rate of 96.5 wt% among numerous solvents[19]. Nonetheless, its low vapour pressure and high residual solvent concentration of 210 ppm restricted its application.

Because of their strong interaction with the bitumen components (saturates, aromatics, resins, asphaltenes), aromatic or cyclic solvents can provide excellent bitumen recovery rates. Noorjahan et al. concluded that cycloalkanes are effective in NAE due to their high solvent-solute interaction, high vapour pressure, and low odour[20]. Nikakhtari et al. evaluated a variety of light hydrocarbon solvents, such as aromatics, cycloalkanes, biologically derived solvents, and solvent mixtures. They concluded that cyclohexane was the best candidate solvent for the following reasons: high bitumen recovery rate of 94.4%±1.7, fine solids content in the recovered bitumen of 1.4%, a removal or drying rate from the extraction tailings of 0.0264 g/(g.min) at ambient conditions, and a residual concentration of 5 mg for every 1 kg of extraction tailings[18]. It is noteworthy to mention that the bitumen recovery rate using cyclohexane as a solvent in this study was one of the highest among other solvents, while the residual solvent concentration along with the removal rate were one of the lowest. The study also concluded that isoprene and its mixtures showed comparable results and can be counted as a second alternative for

NAE. Similarly, Wang et al. found that cyclohexane is an efficient solvent for bitumen extraction because it offers high bitumen recovery rates along with low solvent use, resulting in lower energy intake[21]. Therefore, the solvent used in this research was cyclohexane.

Furthermore, the solubility parameter of the solvent is an essential aspect to consider in NAE techniques. Solubility parameters determine the solvation power of a solvent, and materials with comparable solubility parameters will be able to interact with each other, resulting in miscibility or solvation. The extraction of bitumen using solvents can be viewed from a thermodynamic perspective as a mixing and dissolving process between the solvent and bitumen.

Solubility parameters of bitumen were first determined using Hildebrand solubility parameters shown in Equation (1):

$$\delta T = (e_{coh})^{\frac{1}{2}} = \left(\frac{H_{vap} - RT}{V}\right)^{\frac{1}{2}} \tag{1}$$

δ_T - Hildebrand solubility parameter of solvent

e_{coh} - Cohesive energy density, which is the amount of energy needed to remove unit volume of molecules to infinite separation.

ΔH^{vap} - Heat of vaporization, which is the amount of energy added to liquid to transform it into gas.

R - Gas constant

T - Absolute temperature

V - molar volume.

Any two liquids will be miscible in each other when the solubility parameter between them is small because the resulting enthalpy of mixing (ΔH^{mix}) will be small as illustrated in Equation (2):

$$\Delta H^{mix} = V_m * \varphi_s * \varphi_a * (\delta_s - \delta_a)^2 \tag{2}$$

ΔH^{mix} - Enthalpy of mixing

V_m - Molar volume of the solution

φ_s and φ_a - Volume fractions of solvent and solute, respectively

δ_s and δ_a - Solubility parameters of the solvent and solute, respectively.

Redelius investigated solubility data for different bitumen samples and discovered that the Hildebrand solubility parameter does not accurately predict the solubility of bitumen with solvents[22]. This is attributed to the fact that the Hildebrand solubility parameter only considers dispersion forces and therefore, its prediction for systems with certain molecular interactions other than dispersion forces is inaccurate. Hence, the Hildebrand solubility parameter is unsuitable for molecules with molecular interactions other than dispersion forces. Hagen et. al found that using two-dimensional solubility parameters gives a reasonably fair estimation of the solubility properties, but the best estimation for bitumen was given by the Hansen three-dimensional solubility parameter.[23,24]

Redelius studied the same data set of bitumen to investigate whether Hansen solubility parameter gives a better model for bitumen solubility when compared to Hildebrand solubility parameters. The three-dimensional model included dispersion (D), polar (P), and hydrogen (H) interactions as shown in Equation 3. The study showed that Hansen solubility parameter estimate is specifically accurate for understanding the true nature of bitumen and predicting the solubility of bitumen in different solvents. He also found that the good solvents are found in the region of high dispersion, low polar and hydrogen interactions.[22]

$$\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \tag{3}$$

Non-aqueous extraction techniques have not been executed on a commercial scale despite their promising outcomes. This is due to the complexity in removing solvents from the extracted gangue while maintaining high bitumen recovery rates[18]. Currently, the only regulation regarding allowable amount of solvent loss in tailings is attributed to tailings of froth treatment in hot water extraction, which allows up to 4 volumes of solvent loss per 1000 volumes of bitumen produced[3]. Studies on the removal of solvent from solvent-extracted gangue have used this as their basis, which translates to approximately a solvent mass concentration of 260 ppm in the gangue, i.e., 260 mg of residual solvent per kg of gangue, for a medium grade ore with 10 wt% bitumen.[18,20]

It is understood that coarse particles cause no issues for either aqueous or non-aqueous extraction techniques.[25] However, fine particles, especially clay minerals, are harmful when extracting bitumen using water-based techniques.[25] Clay decreases bitumen recovery rates by slime coating of bitumen droplets.[3] Bitumen recovery rates generally decline with increasing fine particles content. In addition, migration of fine particles to the bitumen produced through water-based techniques lowers the quality of the product bitumen. A high fines migration into the bitumen product requires additional expenses to remove the solids to fulfil pipeline criteria for transport. Furthermore, fine particles are involved in tailings management as well. In tailings ponds, clay is the main contributor of mature fine tailings (MFT), constituting 13% of MFT. If the water is left untreated, it would take decades for these fine particles to settle.[3] As previously mentioned, management of tailing ponds are one of the most complex environmental issues facing the oil sands industry.

Although the majority of fine solids are retained in the gangue after non-aqueous extraction, a significant portion of fine solids also migrate into the product bitumen.[26] The effect of fine solids in the extraction gangue is not completely understood, though they are thought to contribute to the poor recovery of non-aqueous solvents from the extraction gangue.[25] Similarly, the role of fine particles on the recovery of solvent from gangue in non-aqueous extraction techniques has not been extensively researched.

1.5 Drying of Oil Sands Gangue

Even though the solvent extraction technique has been extensively researched, it has not been executed on a commercial level. The challenge remains in removing the residual solvent used during the extraction process from the produced gangue, all while maintaining a high bitumen recovery rate[18]. Solvent removal from the gangue is essential to the economics of the non-aqueous extraction technique and for the environmental impact. The significance of solvent removal not only relies in preventing the release of the organic solvent to the environment, but also in making the NAE technique economically viable since most suitable organic solvents are more expensive than bitumen. Therefore, the residual solvent in the gangue must be minimised as much as possible before releasing the gangue back to the mining site. Solvent removal requires a drying process in which the volatile solvent is evaporated from the gangue in the presence of water. Drying of a cyclohexane-extracted gangue provides an example of drying of two immiscible liquid phases (cyclohexane and water) in a porous solid matrix[27].

The gangue after extraction is a mixture of porous clay/sand solids, a low concentration of residual bitumen, a significant amount of solvent, and a low amount of water. The water in this porous solid matrix forms an immobile phase in the presence of cyclohexane[28].

1.5.1 Air-drying of Reconstituted Gangue

Numerous studies have been conducted to dry solvent-extracted gangue using an air-drying method at ambient conditions. Panda explored the effects of residual bitumen and initial cyclohexane content on the removal of cyclohexane from Alberta oil sands gangue. He developed a protocol to prepare NAE gangue on a lab scale, also called reconstituted gangue.[29] The reconstituted gangue samples had controllable and known compositions where the contents of residual bitumen and cyclohexane were varied. The prepared reconstituted gangue samples were then dried at ambient temperature and pressure for 2 hours at several bed heights. During the drying experiment, residual bitumen in the gangue migrated to the top of the sample and formed a dark, bitumen rich layer. The drying experiment revealed that a higher residual bitumen content caused slower cyclohexane removal. This was due to decreased sorptivity since the viscosity increased when bitumen was dissolved in cyclohexane. Reconstituted gangue sample with 8 wt.% initial cyclohexane was observed to have lower bitumen migration when compared to the sample with 12 wt.% cyclohexane. Panda concluded that in order to achieve residual cyclohexane of less than 260 ppm after 2 hours of drying at ambient conditions, residual bitumen must be less than 1.8 wt.% and the bed height should be less than 1 cm.

Ejike investigated the role of fine solids in the solvent recovery of reconstituted Alberta oil sands gangue using the protocol developed by Panda. Drying experiments were performed at ambient conditions for 2 hours with reconstituted gangue samples prepared using rich-grade solids (10% fines) or low-grade solids (~20% fines) in combination with 12 wt.% cyclohexane or 12 wt.% cyclohexane and 3.7 wt.% water. Reconstituted gangue samples containing only cyclohexane showed two types of distinct drying stages. The first drying stage corresponded to stage 1 evaporation where cyclohexane liquid films maintained hydraulic connectivity to the external surface. The second stage occurred when capillary connectivity was lost, and mass transfer was limited by diffusion of cyclohexane through the porous gangue. For samples containing water, a third drying stage type dominated by water diffusion followed the solvent dominated stage. The study also showed that particle size distribution and gangue wettability depended on the fraction of fine solids, and an increase in fines content resulted in the increase of solvent retention and reduction of solvent recovery.[30]

Following Panda and Ejike, Khalkhali investigated the role of gangue composition on its drying at ambient conditions. Reconstituted gangue samples were prepared with varying bitumen, water, and fines content. Additionally, samples with 1 M NaCl and n-butanol were also studied to further investigate the role of water. The study found that increasing bitumen caused a decrease in the initial drying rate. In addition, doubling water content from 6 wt.% to 12 wt.% resulted in a 60% decease in the initial drying rate, but the complete elimination of water (0 wt.%) also resulted in reduced initial evaporative flux. It is believed that the high water content hindered the formation of cyclohexane films, while the removal of water reduced the average thickness of the films; both decreased the rate of cyclohexane removal. The addition of NaCl showed no effect on drying, while replacing water with n-butanol resulted in a slower initial drying rate. In addition, increasing the fraction of fine solids had no major effect on the initial drying rate.[31]

Comparably, Kuang examined the effect of an induced convective current on the drying of reconstituted gangue at ambient temperature and pressure. Reconstituted gangue samples were prepared with known bitumen, water, and cyclohexane fractions. The horizontal air velocity was ranged from 0.9 to 3.5 m/s and the drying experiment continued for two hours. Reconstituted gangue samples with bitumen content ranging from 0 to 2 wt.% Bit. C were prepared in addition to reconstituted gangue samples with water content ranging from 0 to 8 wt.% water. For reconstituted gangue samples with varying bitumen content, increasing air velocity was observed to increase the average evaporative flux of cyclohexane over the first 10 minutes of drying. The initial flux became independent of air velocity after the exposure to an induced convective current. Moreover, for reconstituted gangue samples with varying water content, the initial flux was the lowest for samples without water at any given air velocity. This outcome indicated that the presence of water increases cyclohexane removal. The highest initial flux values were exhibited by reconstituted gangue samples with 6 wt.% water and 12% cyclohexane at any given air velocity, including ambient air velocity. This may be the ideal amount of water that maximizes cyclohexane liquid film thickness and stability.[32]

It has been shown that at the initial air-drying stage, the liquid connectivity of cyclohexane within the gangue accounts for the rapid, constant, and linear drying rate. This can be attributed to the fact that at the beginning of the drying process, there is enough cyclohexane (liquid) inside the porous gangue for the formation of liquid films, and cyclohexane is transferred by capillary forces through liquid films all the way to the evaporating surface of the reconstituted gangue samples. If the liquid connectivity of cyclohexane throughout the reconstituted gangue sample exists, the film flow will drive cyclohexane to the surface where it can evaporate with a rate close to its free liquid evaporation. Additionally, when cyclohexane is on the exposed gangue surface, the molecules are allowed to escape and form vapor molecules, which makes the drying process fast and similar to any liquid evaporation process. Thus, the initial stage of drying is dominated by the evaporation of cyclohexane and has the major significance of more efficient removal of the cyclohexane under ambient conditions and minimal energy input.

However, the removal of cyclohexane in the final stage of evaporation is significantly slow and its removal requires more energy input. The evaporation of cyclohexane when liquid film connectivity is lost in the final stage, requires higher amounts of energy. In addition to cyclohexane evaporation being slow due to loss of liquid film connectivity, the residual cyclohexane in the gangue needs to diffuse out of the tortuous path of pores, which is also a very slow process.

It has been shown before that increasing temperature and applying vacuum in the initial stage is much less effective than the final stage. Renaud studied the drying of gangue samples at different temperatures and pressures. The study revealed that the removal of the bulk of solvent in the initial stage of drying is less accelerated by the increase in temperature. On the other hand, removing residual solvent in the later stages of drying is enhanced when temperature is increased. Since the use of both high temperature and vacuum was energy intensive, bitumen migration phenomena inside the porous gangue bed and its effect on drying was investigated under ambient conditions.[33]

The major advantage of the air-drying method is that it requires minimal energy input. This is attributed to the fact that the initial drying stage is substantially fast at ambient conditions, and cyclohexane evaporates at this stage with a rate close to that of steady state pure liquid evaporation. Therefore, there is no need for any energy input at the initial drying stage. Furthermore, despite the numerous experiments conducted on how the key gangue components affect the removal of cyclohexane using an air-drying method under ambient conditions, using only this drying method was observed to have significant drawbacks. Air-drying of reconstituted gangue samples was insufficient for the removal of cyclohexane from the gangue in all of the experiments performed. The process was also slow because liquid cyclohexane in the gangue initially flows upwards due to capillary pressure to the gangue surface before it vaporizes as discussed above. For instance, when 25 g of reconstituted gangue samples with 1 cm bed height were dried at room temperature for two consecutive hours, the residual cyclohexane content in the gangue was a few hundred ppm[29].

1.5.2 Conventional Heating of Reconstituted Gangue

A typical gangue sample consists of primarily sand and clay particles (80 – 90 wt%), along with solids, water, residual bitumen along with the residual solvent. The entire gangue sample will be heated when conventional heating is utilised to remove cyclohexane from the gangue, including the solids. It is critical to mention that heating the solids component of the gangue is unnecessary and cannot be prevented in conventional heating. When conventional heating methods are utilised to treat cyclohexane-extracted gangue, the use of thermal energy will be required. Therefore, it can be determined that employing conventional heating methods to remove cyclohexane from NAE gangue is inconsistent with why solvent extraction techniques are preferred.[31] Furthermore, the component of interest to be heated is cyclohexane, and directing heat towards only one component of the gangue will consume less time and energy. For this reason, the use of a selective method will be faster, more energy efficient, and aid towards commercialising the NAE techniques.

NAE would be as energy intensive as water-based extraction if cyclohexane is to be removed by heating the entire sample. However, this can be avoided due to the presence of film flow. The initial drying stage is fast at room temperature and pressure as demonstrated by numerous researchers. Therefore, any external energy input by raising the temperature or applying vacuum for improved removal of solvent from the gangue is not necessary until the initial drying stage is done.

Moreover, air-drying demands long heating periods and leaves behind high residual cyclohexane concentrations, while conventional heating leads to substantial energy losses due to its non-selective nature. To overcome the limitations of air-drying and conventional heating methods, utilising a selective method of heating along with air-drying is an attractive alternative that will assist in the process of cyclohexane removal from the gangue. Considering that the initial stage of air-drying is cyclohexane-dominated vaporization at the surface of the gangue, air-drying will be performed for the first 30 minutes prior to heating the reconstituted gangue samples in microwave in the final stage of drying. This will further reduce the time and energy needed for the removal of cyclohexane from the gangue since air-drying has the advantage of a fast initial drying stage at ambient conditions along with minimal energy input.

The final stage of drying, however, is dominated by water evaporation, and cyclohexane evaporation is an order of magnitude slower at ambient temperatures when compared to the initial stage of drying[28-32]. During this stage of drying, selective heating is an attractive method to remove cyclohexane from the gangue.

1.5.3 Microwave Heating of Reconstituted Gangue

Recent research has investigated how various factors affect the recovery of cyclohexane from the gangue, but most of the studies utilized an air-drying method only. Microwave heating is considered as a selective method which has substantial advantages over air-drying and conventional heating. This unconventional heating mechanism transfers energy directly to microwave-absorbing materials, creating a fast and more energy-efficient drying process.[34] The process through which materials are heated in a microwave is significantly different from conventional ovens. Heat is generated internally by the material during microwave heating rather than from an external heating source. For this reason, the direction of heat flow in microwaves is the opposite of that in materials heated conventionally.[35]

The energy efficiency and short heating periods of microwave heating have been demonstrated by numerous researchers.[36-39] Halder et al. contrasted conventional and microwave heating in the processing of bulk glass and found that the electrical power consumed in microwave and conventional heating were 5 kWh and 14 kWh, respectively.[40] Wei et al. studied the heating results of concrete under microwave and conventional heating processes. The total time required to achieve a temperature of 500°C with microwave and furnace heating were 5.1 min and 32.6 min, respectively. In addition, the energy consumption and heating time were only 1/16 and 1/6, respectively, of conventional furnace heating.[41]

Moreover, the removal of organic pollutants from soils by means of microwave heating has been demonstrated as a substitute for traditional thermal desorption procedures. Robinson et al. studied the microwave treatment of soils contaminated with heavy and light-hydrocarbons and demonstrated that microwave treatment is shown to eliminate Poly-Aromatic Hydrocarbons (PAHs) from both the heavy and light-contaminated soils. The study revealed that more than 95% PAH removal can be achieved under moderate processing conditions[42]. Horikoshi et al showed that considerable trichloroethylene removal from a model soil material was achievable.[43] Yuan et al. studied the remediation of hexachlorobenzene (HCB) contaminated soils by microwave radiation in a sealed vial. The study revealed that water itself contained in the damp soil may act as microwave absorber and remediate the contaminated soil without addition of any other microwave absorbers and that the treatment of practical HCB contaminated soil by microwave reduced HCB from 55.8 mg/kg to 0.91 mg/kg.[44]

In terms of removing cyclohexane from reconstituted gangue using microwave technology, this approach was perceived as a solution for long drying times and energy intensity associated with the removal of cyclohexane from NAE gangue. Khalkhali et. al demonstrated that microwave heating can be an effective means for removing cyclohexane from oil sands gangue in the presence of water.[45] Reconstituted gangue samples were prepared with same amounts of solid particles, residual bitumen (1.15%), and cyclohexane (12%) but different water contents (4 wt%, 6 wt%, and 12 wt%) then heated in a laboratory microwave instrument. The study found that microwave heating was rapid, cyclohexane was completely removed in only 8 minutes, and that 6 wt% water was sufficient to remove 12 wt% of liquid cyclohexane present in the reconstituted gangue samples. It is significant to mention that there has not been much work done on the effect of residual bitumen, cyclohexane, or fine content on the removal of cyclohexane from reconstituted gangue using microwave selective heating. Experimental data showed that microwave heating could be an alternative option over conventional heating approaches when treating contaminated soils that contain strong dielectric characteristics[46]. Thus, gangue or reconstituted gangue serves as a perfect example for contaminated soil containing a dielectric material (water).

1.6 Microwave Technology

1.6.1 Historical development

Microwaves are electromagnetic waves with a frequency between 0.3 GHz and 30 GHz and a wavelength between 1 mm and 1 m[47]. While 2450 MHz microwave generators are typically utilised in Europe, 915 MHz generators are employed in the United Kingdom and North America. Maxwell's equation predicted the idea of microwaves in 1864, and Heinrich Hertz later demonstrated it in 1888. During World War II, a significant advancement in this subject was initiated. Microwave ovens gained popularity in 1951 as rapid and efficient heaters. Microwave ovens were later redesigned by Japanese engineers to be more affordable, dependable, and user-friendly.[48]

1.6.2 Working principle

Microwaves are a form of electromagnetic radiation; that is, they are waves of electrical and magnetic energy moving together. Electromagnetic waves cover a broad spectrum from long radio waves to short gamma rays. Microwave technology has practical applications in cellular phones, RADAR, satellites, and medical equipment. Materials can be divided into three groups based on their capability to be heated by microwaves: conductors, insulators, and absorbers. Figure 6 demonstrates the microwave absorption properties of various materials.

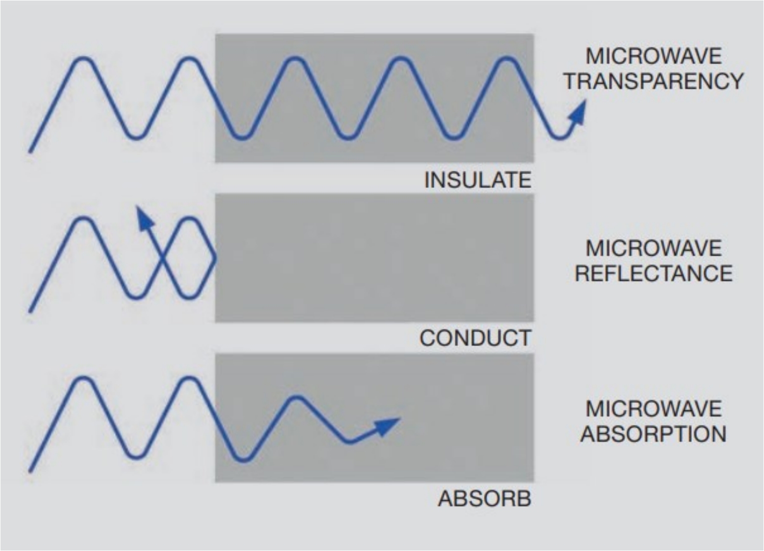

Figure 6. Microwave absorption properties of materials. Top to bottom: insulators, conductors, and absorbers.[34]

Dielectric polarisation and conduction loss are two factors that microwave heating depend on. Dielectrics are materials with the capability to absorb microwave radiation[49]. The dielectric constant and the dielectric loss are typically two parameters that determine the dielectric characteristics of a material and have been extensively studied. Dielectric constant is the capacity of a molecule to become polarised in an electric field, while dielectric loss is the capacity to convert electromagnetic energy into heat.

Dipolar polarization is responsible for most of the microwave heating in the solvent systems. Dipolar polarization occurs when polar molecules characterized with a dipole moment align themselves in an electromagnetic wave with rapid oscillation.[50] The molecule turns its direction back and forth to align itself with the electromagnetic wave as it alternates. The rotation causes energy to be lost from the dipole to nearby molecules through molecular friction and collisions, giving rise to dielectric heating. For this reason, microwave heating is called dielectric heating. Dipoles collide with the adjacent molecules, which causes agitation and generation of heat. Therefore, microwave radiation can heat materials containing a diploe.

One of the key differences between microwave drying and other drying methods is that the energy in microwave heating is transmitted directly towards the dipole molecule. The direct energy transfer from microwaves to dipole molecules implies that materials containing dipole molecules, such as water, have the capacity to absorb the bulk of the electromagnetic energy at microwave frequencies. Compared with conventional heating techniques, microwave heating has the following advantages: higher heating rates, shorter drying time, selective heating, and greater control of the heating process.

1.7 Research Intent

Non-aqueous extraction of Alberta oil sands has been extensively investigated, and the barrier that has been acknowledged was the solvent losses to the extraction gangue. The removal of valuable solvent from the gangue material is a significant aspect of NAE, but the factors influencing solvent recovery from extracted gangue are yet to be understood. Previous researchers have studied the effects of temperature, bitumen, fines, and solid content on the recovery of cyclohexane from the extracted gangue using an air-drying method. Other effects such as the introduction of a convective current induced by a fan have also been studied. The gap of knowledge on the influence of microwave heating on the removal of cyclohexane in non-aqueous extracted gangue led to the current study. In this research, reconstituted gangue samples with different contents of fine particles were prepared and the effect of microwave heating along with a hybrid method of air-drying coupled with microwave heating was studied. An understanding of the cyclohexane removal process can lead to a more accurate system modelling as well as mitigate one of the most significant issues with NAE and aid its commercialization.

2. Methodology

2.1. Criteria for the Reconstituted Gangue

Gangue is the waste material obtained post-extraction in an industrial scale. It is a solid mixture consisting of sand, residual bitumen, solvent, and any water initially in the oil sand ore. In industry, the valuable solvent must be separated and recovered from the gangue material in order to be able to re-use it in other extractions and minimize its environmental toxicity. Reconstituted gangue, on the other hand, is a synthetic gangue material that mimics the characteristics of the gangue obtained after the solvent extraction process. The composition of reconstituted gangue can be controlled and examined depending on the parameters of interest.

The composition of oil sands ore can vary depending on location and grade. Consequently, each batch of non-aqueous extraction of oil sand ore produces a gangue of different composition of sand, residual bitumen, solvent, and water[33]. This variability creates a problem when analyzing the gangue because it becomes complicated to determine the effect of every component on the solvent recovery process. In addition, any systematic study of a process necessitates clearly defined parameters for accurate analysis. To address this issue and to control the composition of the gangue, artificial or reconstituted gangue samples with known compositions were prepared. Therefore, the effect of each component on the solvent recovery process can be evident. Reconstituted gangue samples were prepared based on the parameter being studied. In this research, bitumen, water, and cyclohexane were added in controlled amounts to solids obtained from Dean-Stark Extraction.

The basis for the preparation of reconstituted gangue was outlined in a study completed by Panda. The study compared the drying behaviour of reconstituted gangue with real extracted gangues to confirm their comparable behaviour; drying results from both reconstituted and real gangue were similar[29]. It is important to note that the objective was not to prepare reconstituted gangue samples that perfectly replicated the characteristics of the real extracted gangue, but to prepare reconstituted gangue samples with controllable parameters that are reflective of the drying behaviour of the real extracted gangue. Thus, conducting solvent recovery experiments on reconstituted gangue samples will help understand the role of the parameter of interest on solvent recovery.

The composition of the reconstituted gangue was prepared based on gangue obtained from NAE of rich-grade Athabasca oil sands. Residual bitumen content in the extracted gangue depended on the extraction process, but ideally should be above 96 wt.%. Water content in the extraction gangue ranged from 0 to 12 wt.%, which was approximately the amount initially present as connate water in the oil sands ore[51]. In addition, the cyclohexane content ranged from 8 to 18 wt.%, with an average of 11.8 ± 2.1 wt.%.[33]

Based on the composition of the extracted gangue obtained from non-aqueous extraction of rich-grade oil sands, the reconstituted gangue samples used in this research were prepared to the following specifications:

- Residual bitumen content at 1 wt.%
- Fine particles content at 0, 10, and 20 wt.%
- Cyclohexane content at 12 wt.%

2.2 Materials Used

Syncrude Canada Limited provided the high-grade oil sands ore used in this research. The solvent used in this study (cyclohexane) is a certified ACS grade and was obtained from Fischer Scientific USA. Cyclohexane was used during the Dean-Stark extraction and for the preparation of reconstituted gangue samples. Demineralized water was also required to prepare reconstituted gangue samples. Oil sand samples were milled to homogenize the sample prior to Dean-Stark extraction.

2.3 Dean-Stark Extraction

The Dean-Stark extraction is a procedure to determine the fluid saturation of a sample through vaporizing it with a boiling solvent[52], followed by water condensation and collection in a calibrated trap, as illustrated in Figure 7.

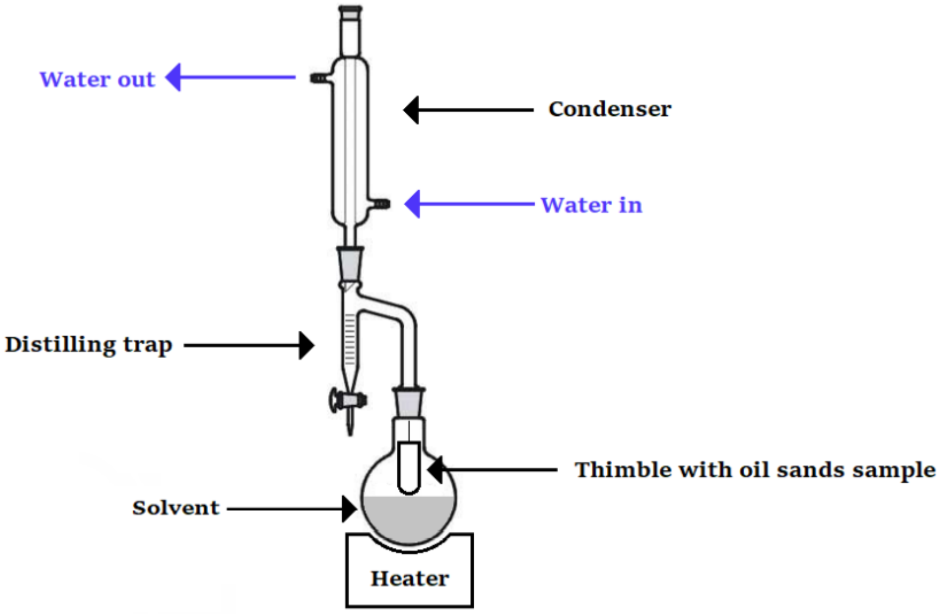

Figure 7. Schematic of Dean-Stark Extraction Apparatus.

Dean-Stark extraction was performed to separate the solids for the preparation of reconstituted gangue and to determine the composition of the initial oil sands sample. Approximately 100 g of oil sands sample was crushed and placed into a pre-weighted extraction thimble. The thimble was then placed on a wire holder, which was suspended in the neck of a round bottom flask from an adaptor as shown in Figure 7. The adaptor connected the round bottom flask, containing roughly 250 mL of cyclohexane, to a condenser, which was equipped with a graduated distilling trap. Cyclohexane was heated using a round bottom flask heater, it then vaporized and refluxed through the system and dissolved bitumen into the round bottom flask. Cold water flowed through the condenser to condense both cyclohexane and water vapor then drained out. The connate water present in the oil sands sample vaporized, and subsequently condensed and collected in the distilling trap, while mineral solids remained in the thimble. A standard Dean-stark extraction requires 3 to 4 hours. However, all extractions were left to run for 24 hours to ensure the complete removal of bitumen, therefore producing bitumen-free solids that were later used for the preparation of reconstituted gangue. A total of 15 extractions were done to prepare the reconstituted gangue samples in this study.

The extractions were stopped when the solvent dripping out of the thimble was clear. At the end of the Dean-Stark extraction, all connate water was collected in the distillation trap, bitumen was dissolved in cyclohexane and collected at the bottom of the flask, and solids were trapped in the thimble. The solids obtained post extraction consist of a mixture of fine and coarse solids and will hereafter be called Soxhlet solids. Fine solids were contained in the Soxhlet solids, trapped inside the pores of the extraction thimble, and in the bitumen solution during Dean-Stark extraction. Although a small amount of fine solids migrated into the bitumen/cyclohexane solution, the amount is less than 1% of the total oil sands solids originally in the sample, making it negligible. The amount of connate water can be read from the calibrated trap and bitumen content can be determined by mass balance given that the weight of the initial oil sands sample and weight of the extracted mineral solids and water are known.

Next, the composition of the initial oil sands sample was determined by dividing the amount of each individual component obtained at the end of the extraction by the weight of the original oil sands sample. In addition, to determine the amount of fine particles in the initial oil sands sample, the dry Soxhlet solids were sieved using a 45 µm aperture in order to separate fine solids, and the extraction thimble was weighed after the discharge of soxhlet solids in order to measure the weight of fine solids trapped in the pores of the thimble (the thimble is also weighed before dean stark extraction). After all, fines content in the oil sands sample was calculated as the weight of fine solids separated by sieving plus the weight of fine solids trapped in the pores of extraction thimble divided by the total weight of solids collected after Dean-Stark extraction, i.e. Soxhlet solids. Fine solids were later mixed again with coarse solids to desired proportions, before the preparation of reconstituted gangue.

2.4 Preparation of Reconstituted Gangue

The reconstituted gangue samples were made up of the same components as the real extracted gangue. In this study, reconstituted gangue samples were prepared using dry Soxhlet solids, bitumen, demineralized water, and cyclohexane. Soxhlet solids (mixture of coarse and fine solids) were collected from the Dean-stark extractions after drying and used as the base material for making the reconstituted gangue samples. The composition of the Soxhlet gangue was assumed to be representative of the solids initially present in the oil sand ore. All bitumen-associated carbon was assumed to have been removed during Dean-Stark extraction due to the high solubility of bitumen in cyclohexane, leaving behind only inorganic sources. CHNS analysis was used to measure the carbon content of the Soxhlet gangue, also known as inorganic carbon. The Bit. C content for a sample of DSBS can be determined by subtracting the inorganic content of Soxhlet solids from the carbon content obtained from CHNS analysis.

Soxhlet solids obtained directly after Dean-Stark extraction were cyclohexane-wetted. To ensure that the Soxhlet solids were entirely cyclohexane-free, the solids were first dried at ambient conditions (21.5°C and 1 atm) under the fume hood for 2 hours before being placed in the vacuum oven (85°C and 30 mbar) for 12 hours. The dry Soxhlet solids were then passed through a 500 μm mechanical sieve to remove particles with 500 μm diameter or larger from the Soxhlet solids. At this point, Soxhlet solids were dry, bitumen-free, and ready to be mixed with known amounts of bitumen, water, and cyclohexane.

Assumptions made when preparing reconstituted gangue:

- The composition of the Soxhlet gangue represents the solids initially present in the oil sand ore.
- Due to the mixing and sieving; bitumen, water, and cyclohexane will be uniformly distributed in the reconstituted gangue and the final product should be almost homogeneous.[18]
- All bitumen associated carbon have been removed during Dean-Stark extraction because bitumen is highly soluble in cyclohexane, and only inorganic sources are left behind.

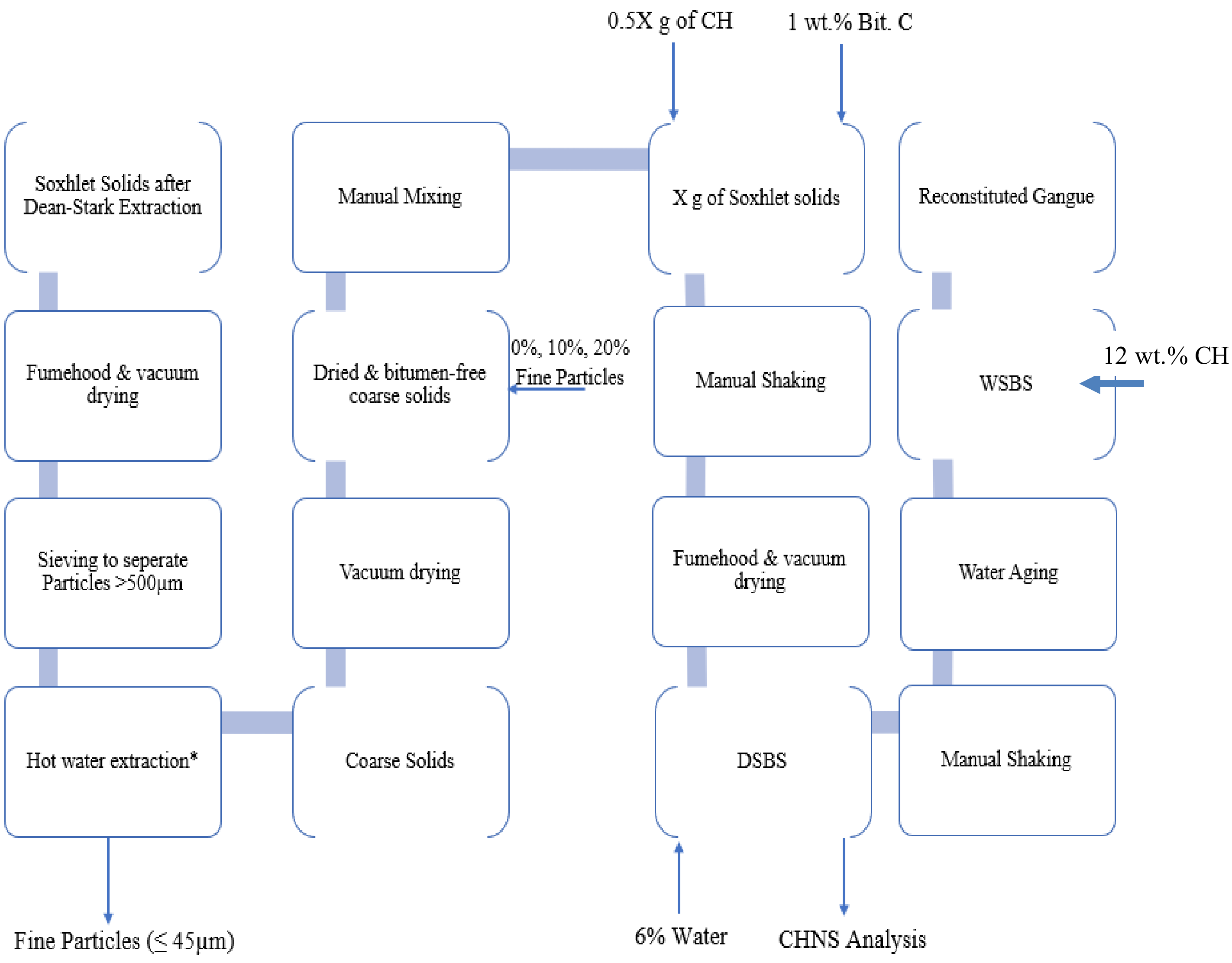

Figure 8. Flowchart for Preparation of Reconstituted Gangue. (CH = cyclohexane)

*Detailed in Section 2.5

2.4.1 Addition of Bitumen

Due to the viscous nature of pure bitumen, it was added to the dry Soxhlet solids in a cyclohexane solution. Adding bitumen solution to the Soxhlet solids instead of pure bitumen prevented clumping and aided the bitumen to be uniformly distributed in the gangue. The amount of cyclohexane used to make the solution was half the weight of the Soxhlet gangue; First, cyclohexane was added to a 500 mL Teflon bottle with the target amount of bitumen and manually shaken until the bitumen was completely dissolved. It is important to mention that the mass of bitumen added depends on the target Bit. C wt.% and the amount of Soxhlet solids used. Then, the dry Soxhlet solids were added to the solution in the Teflon bottle and mixed. Next, a slurry containing bitumen, cyclohexane, and Soxhlet solids was formed. In order to prevent bitumen from migrating with cyclohexane through the solids and deposit on the surface of the gangue, the slurry was poured into a large Pyrex glass dish and manually mixed for 1 hour on a continuous basis. This step also ensured that bitumen was uniformly distributed throughout the slurry. After that, the glass dish was placed in a vacuum oven (85°C and 30 mbar) for 2 hours to guarantee the complete removal of cyclohexane. The reason why cyclohexane was removed is because it was initially only added to facilitate the bitumen mixing into the Soxhlet solids, meaning that the amount added previously did not represent the required amount needed to prepare reconstituted gangue. Finally, the resulting solids were evenly coated with the desirable amount of bitumen and were referred to as Dry Soxhlet Bitumen Solids or DSBS. To verify the bitumen content of DSBS and to determine if bitumen was evenly coated in the Soxhlet solids, a small amount of DSBS was examined using CHNS analysis before adding water and cyclohexane.

2.4.2 Addition of Water

First, the previously obtained DSBS was weighed and transferred into a clean 500 mL Teflon bottle and water was then added based on the target mass percent of water (6%) and the weight of DSBS. Then, the contents of the bottle were mixed for 20 minutes to ensure uniformity of the mixture. At this point, water added to the mixture needs time to enter the pores of DSBS and imitate the distribution of water in the real industrial gangue. For this reason, the mixture was left to age for 24 hours[29] in a tightly sealed bottle with Parafilm. This process is called water ageing. Finally, the product obtained at the end of this step contains Soxhlet solids, bitumen, water, and is termed Wet Soxhlet Bitumen Solids WSBS.

2.4.3 Addition of Cyclohexane

The amount of cyclohexane to be added to WSBS depends on the mass of WSBS and the target mass percent of cyclohexane, which was 12%. The gangue obtained from non-aqueous extraction of oil sands had an average of 11.8 ± 2.1 wt.%[33]. Furthermore, WSBS was transferred to a clean bottle and the target cyclohexane amount was immediately weighed, added to the WSBS, and sealed using Parafilm. This step was done quickly due to the volatile nature of cyclohexane. The contents of the bottle were then mixed for 20 minutes. Lastly, the product obtained at the end of this step contained Soxhlet solids, bitumen, water, cyclohexane, and was termed reconstituted gangue. The prepared reconstituted gangue samples were then used immediately for the drying experiments.

Panda determined that the critical surface tension of Soxhlet solids obtained from rich-grade Athabasca oil sands is 34±7[29]. For temperatures ranging from 20 to 25 °C, the surface tension of cyclohexane is 24.9-24.4 mN/m[53], while the surface tension of water is 72.8 - 72 mN/m[54]. It follows that only cyclohexane will wet the reconstituted gangue while water will not be able to. This is because the critical surface tension for Soxhlet solids is higher than the surface tension of cyclohexane but lower than that of water. This was further demonstrated by the penetration of cyclohexane into the Soxhlet solids in contrast to the formation of water droplets on the surface of the Soxhlet solids.

2.5 Extraction of Fine Solids from Soxhlet Solids

Fine solids were extracted from the dry Soxhlet gangue by hot water extraction. Figure 9 shows the flow diagram for the fine extraction procedure. First, Soxhlet solids was placed in a glass beaker and deionized water was then added to the solids. The combination was then mixed for 10 minutes before being placed on top of a heating plate and heated at a temperature of 60°C. Next, the supernatant was transferred onto a 45 µm aperture sieve and shaken for 5 minutes. This process was repeated until the supernatant containing suspended fine particles was clear. About 15-25 repetition of water addition and sieving was required to reach an almost clear supernatant. After that, the solids collected on the sieve were spread out and placed in a vacuum oven at 70°C to evaporate the water and collect the fine solids. The coarse solids (>45µm) remaining in the beaker were also dried in a vacuum oven at the same temperature.

Figure 9. Soxhlet Solids before Fine Extraction.

Figure 10. Soxhlet Solids after Fine Extraction.

Following the separation of fine particles from the Soxhlet solids, fine particles were added back to the Soxhlet in known amounts. First, the target ratio of fine solids in the reconstituted gangue was determined (0%, 10%, 20%). Based on that, the required ratios by mass of fine solids to coarse solids were combined in a Teflon container. The mixture was mixed manually with a spatula for five minutes before it was ready to be used as dry Soxhlet solids in the preparation of reconstituted gangue.

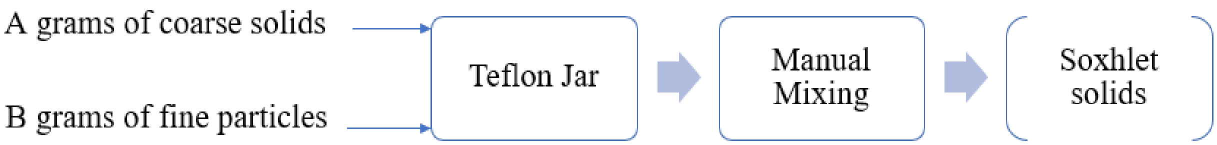

Figure 11. Flowchart for Addition of Fine Particles.

2.6 Samples Prepared

Using the procedure outline previously, two groups of samples were prepared with the specifications outlined in Table 1. Drying experiments in both groups were performed in triplicates.

The effect of fine particles on the evaporation of cyclohexane from reconstituted gangue samples containing constant amounts of bitumen, water, cyclohexane, and varying amounts of fine particles (0%, 10%, 20%) was studies in two different drying mechanisms: Microwave-only (Group A) and air-drying followed by microwave heating (Group B).

Table 1. Composition of Reconstituted Gangue Samples Prepared.

Drying Mechanism	Bitumen Content (wt.%)	Water Content (wt.%)	Cyclohexane Content (wt.%)	Fine Particles Content (wt.%)
Group A: Microwave only	1	6	12	0, 10, 20
Group B: Air-drying + microwave	1	6	12	0, 10, 20

2.7 Sample Packing

A gangue sample, reconstituted or extracted, consists of Soxhlet solids with bitumen, water, and cyclohexane. For samples undergoing microwave heating, approximately 5 ± 0.04 g of reconstituted gangue samples were directly packed into a glass vial (Fisher Scientific, height = 4 cm, OD = 1.3 cm). All samples were compactly packed to a constant height of 1.5 ± 0.09 to ensure consistent microwave heating among different samples.

Air-drying experiment was done prior to microwave heating for samples in Group B. Approximately 25.0 ± 0.07 g of reconstituted gangue was weighted onto a glass petri dish (5 cm ID, 6 cm OD, 1.5 cm height, PYREX CLS316060). By maintaining the same mass, bed height and bed radius, the bulk density (ρ_{bulk}) and average porosity of the sample were kept constant.

The bulk density of the packed bed can be calculated as

$$\rho_{bulk} = \frac{mass\ of\ solid\ in\ the\ packed\ bed}{volume\ occupied\ by\ the\ bed} \tag{4}$$

The average porosity can be calculated as

$$\phi = 1 - \frac{\rho_{bulk}}{\rho_{particle}} \tag{5}$$

2.8 Drying Conditions: Air-Drying and Microwave Heating

Air-drying experiments were performed under a fume hood, and the sash height was kept constant to maintain constant air flow. The petri dish was placed on a balance (Model XP203S, Mettler Toledo) and connected to a computer where the balance weight was recorded every 20 seconds using BalanceLink software. All sides of the balance were kept open during the duration of the experiment to enable flow through the sample. All air-drying experiments were performed at room temperature (20 ± 2°C) and samples were dried for 30 minutes.

The microwave heating system used in this study consisted of a laboratory microwave source (MH2.0W-S, National Electronics), 2 kW switch-mode power supply (SM745G.1, Alter), an isolator (National Electronics), a three-stub tuner (National Electronics), a single mode waveguide applicator, and a sliding short. Before each experiment, the tuner, and the sliding short were used to adjust the microwave impedance and maximize the energy transfer to the sample. Applied microwave power was monitored using a dual channel microwave power meter (E4419B, Agilent) and two power sensors (8481A, Agilent) connected to a dual directional coupler with 60 db nominal attenuation (Mega Industries). To avoid interference with the applied microwave, a fiber optic temperature sensor, with a signal conditioner (Reflex signal conditioner, Neoptix) was used to measure the sample temperature during microwave heating. A Labview program (National Instruments) connected to a data acquisition system was used to record microwave applied power and samples temperature during the microwave heating. For each microwave heating experiment approximately 5 grams of reconstituted gangue was packed into a glass vial then placed inside a sample holder. Sample height in the vial was kept at 1.5 cm to guarantee consistent microwave heating among different runs. A 0.5 SLPM stream of air was used to sweep the evaporated water/cyclohexane from the sample holder.

2.9 CHNS Elemental Analysis

An elemental analyzer (Flash 2000 CHNS/0 Analyzer, Thermo Scientific) was used to determine the carbon, hydrogen, nitrogen, and sulfur content of the various gangue samples. Samples were first homogenized using a mortar and pestle before being placed into a tin capsule. Only 10 – 15 mg of sample was required per capsule. The capsules were then loaded into the autosampler of the analyzer and sent to the quartz combustion reactor inside a furnace with a temperature of 900°C. Upon contact with oxygen in the reactor, a strong exothermic reaction was triggered due to the oxidizing environment. Temperatures reached approximately 1800°C and the sample combusted instantly[55]. The resulting combustion products were transported across the reactor and oxidation finalized. Any nitrogen oxides and sulfur trioxides possibly formed would be reduced to nitrogen and sulfur gas. The gas mixture existing in the reactor consisted of CO_2, H_2O, N_2 and SO_2 was then fed into a chromatographic column and separated before being passed through a thermal conductivity detector (TCD). The TCD produces electrical signals which were then processed by the Eager Xperience software to provide the percentages of carbon, hydrogen, nitrogen, and sulfur in the sample. The time required between dropping a sample into the reactor and obtaining the carbon, hydrogen, nitrogen, and sulfur fractions was approximately 12 minutes for each sample. Inorganic or non-bitumen associated carbon can be determined via CHNS analysis of Soxhlet solids. The Bit. C content for a sample of DSBS can be determined by subtracting the inorganic content of Soxhlet solids from the carbon content of DSBS, which can both be obtained from CHNS analysis.

2.10 Residual Cyclohexane Analysis

Samples were introduced into the gas chromatograph (GC) via the headspace technique. The samples were heated and agitated in the auto-sampler to allow the headspace to equilibrate with the sample in the vial. An aliquot of the headspace is injected onto the GC column where the separation of analytes occurs based on compound size, boiling point, and polarity.

The sample was analyzed by Gas Chromatography/Mass Spectrometry (GC/MS). Qualitative determination was performed by comparison of the sample mass spectra to that of the calibration standards and by comparison of their retention time to those of the calibration standards. Analytes are quantified by comparing the response of a major (quantification) ion relative to an internal standard. Reconstituted gangue sample was weighed into a vial to which 10 mL of methanol/O-Xylene-d10 extraction solution was added. After mechanical extraction, a 1mL aliquot of the sample extract was spiked into a Headspace vial containing a matrix modifying solution which contains Internal Standards.

3. Results and Discussions

3.1 Properties of Oil Sands Ore and Gangue

As mentioned previously in Section 2.3, Dean-Stark extraction was used to determine the composition of the oil sands ore used in this research. The results are presented in Table 2. The average and standard deviation values were calculated based on 15 extractions. Bitumen, water, and solids contents of the oil sands ore were calculated based on the total weight of the ore, while the content of fine particles was determined based on the weight of solids.

Table 2. Composition of oil sands ore.

	Bitumen*	Water*	Solids* (< 500 μm)	Fine Particles** (<45 μm)
Content (wt.%)	11.6 ± 0.7	3.1 ± 0.2	84.7 ± 0.6	6.8 ± 0.9

*Based on total oil sands ore weight.

**Based on solids weight only.

The oil sand ore samples used in this research are identical to those used by Kuang and Khalkhali. Analyses revealed nearly identical composition, density, and porosity values[31,32]. Table 3 shows the particle size distribution for Soxhlet solids obtained through sieve analysis while Table 4 shows the particle size distribution for fine particles obtained from [30]. In addition, characteristics of Soxhlet solids used for the preparation of reconstituted gangue are presented in Table 5.

Table 3. Particle Size Distribution for Soxhlet Solids.

	Particle Size (μm)				
Weight Percent (wt.%)	<45	45 – 150	150 – 212	212 – 500	>500 +
	6.63	25.62	48.84	10.66	7.7

Table 4. Particle Size Distribution for Fine Particles of Soxhlet Solids[30]

Sample	Constituent Solid	D10 (μm)	D50 (μm)	D90 (μm)
Rich-grade	Fine Particles (<45μm)	1.6 ± 0.1	9.0 ± 0.9	41.3 ± 3.4

Table 5. Bulk density, particle density, and porosity for Soxhlet solid.[32]

Bulk Density (ρ_{bulk})	1458 ± 22 kg/m^3
Particle Density ($\rho_{particle}$)	2610 ± 68 kg/m^3
Porosity (ϕ)	0.44

3.2 Analysis of Drying Curves

3.2.1 Air-drying Experiment

For samples undergoing air-drying experiment (Group B), the changes in weight of the reconstituted gangue samples over the duration of the drying experiment were recorded automatically every 20 seconds and later used to calculate the cumulative weight loss of samples at different times in the experiment. Generally, when the air-drying experiment is performed for reconstituted gangue samples with cyclohexane, the initial stage of drying is dominated by cyclohexane removal and the evaporative flux will be at its maximum level[18,28]. The early stages of air-drying experiments collectively exhibited maximum evaporation rates as evident from the slope of Figure 12. Cyclohexane liquid films are formed through capillarity during the early stages of evaporation, maintaining hydraulic connectivity to the exposed surface. A significant concentration gradient for cyclohexane exists at the exposed surface, allowing for its fast vaporisation. The presence of liquid films assists in the process of solvent removal by eliminating the need for transport via diffusion, and the initial stage of drying is maintained as long as liquid films remain connected to the open surface.

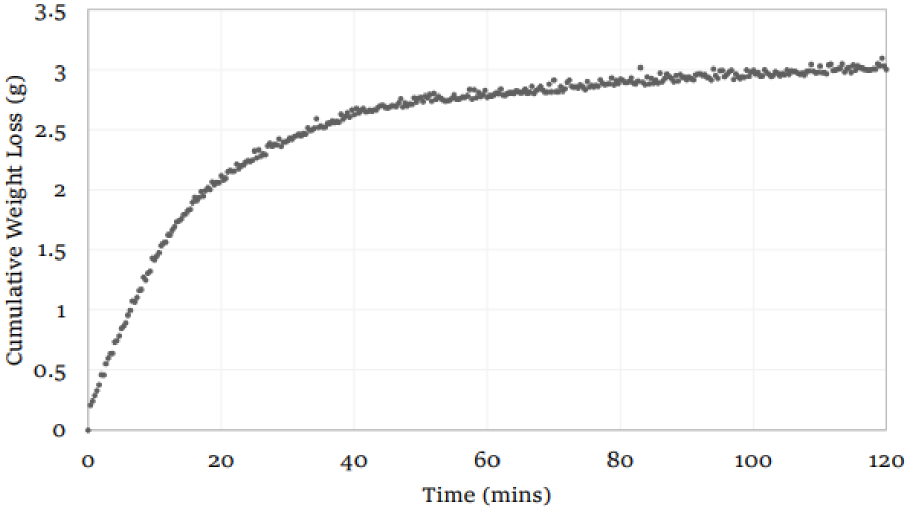

Figure 12. Typical air-drying curve of a reconstituted gangue sample.

The mechanism by which cyclohexane in reconstituted gangue evaporates is that during the initial stage, cyclohexane and bitumen solution move upwards to the surface by capillary forces. After reaching the top of the gangue, cyclohexane evaporates, and bitumen deposits on the top surface creating a distinct layer. This initial stage is known to have fast, constant, and linear mass loss because of the liquid connectivity of the solvent within the porous medium of the gangue[54]. This constant-rate stage lasts approximately if there are sufficient cyclohexane liquid films that saturate the surface of the gangue. Since maximum evaporation rates were seen during the early stages of air-drying experiments, Group B was given approximately 30 minutes of air-drying prior to microwave heating.

To determine the drying flux during the air-drying experiment, the slope of the air-drying curve in the early stages of evaporation was calculated by

$$Evaporation\ flux = \frac{slope\ of\ the\ linear\ regression\ fit}{Surface\ area\ of\ cyclohexane\ evaporation\ (19.64\ cm^2)} \tag{6}$$

It can be deduced from Table 6 that when reconstituted gangue samples containing cyclohexane were given more time under ambient conditions, the evaporation flux decreased by 33% for samples with 0% fine particles and 44% for samples with 10% and 20% fine particles. The decrease in evaporation flux indicates that cyclohexane is evaporating at a slower rate from the reconstituted gangue, however, it is still evaporating from the sample at minimum energy input. Previous experiments with air drying collectively revealed that high evaporation flux occurs at the early periods of air-drying experiments. This is explained by the existence of cyclohexane liquid films and their connectivity to the exposed surface of the reconstituted gangue. After the first 10 minutes of air-drying, a lower cyclohexane evaporation flux is observed. This is since liquid film connectivity inside the reconstituted gangue begins to decrease. The reduction in liquid film connectivity causes the cyclohexane removal process to slow down, and its removal requires more energy input.

Table 6. Cyclohexane evaporation flux for air-drying experiment at different fine contents.

Fine Particles Content (wt. %)	First 10 minutes (600 seconds) ($\frac{g}{second.cm^2}$)	First 20 minutes (1200 seconds) ($\frac{g}{second.cm^2}$)	First 30 minutes (1800 seconds) ($\frac{g}{second.cm^2}$)
0%	$3.56*10^{-5}$	$2.55*10^{-5}$	$2.55*10^{-5}$
10%	$5.60*10^{-5}$	$4.07*10^{-5}$	$3.56*10^{-5}$
20%	$5.60*10^{-5}$	$4.07*10^{-5}$	$3.56*10^{-5}$

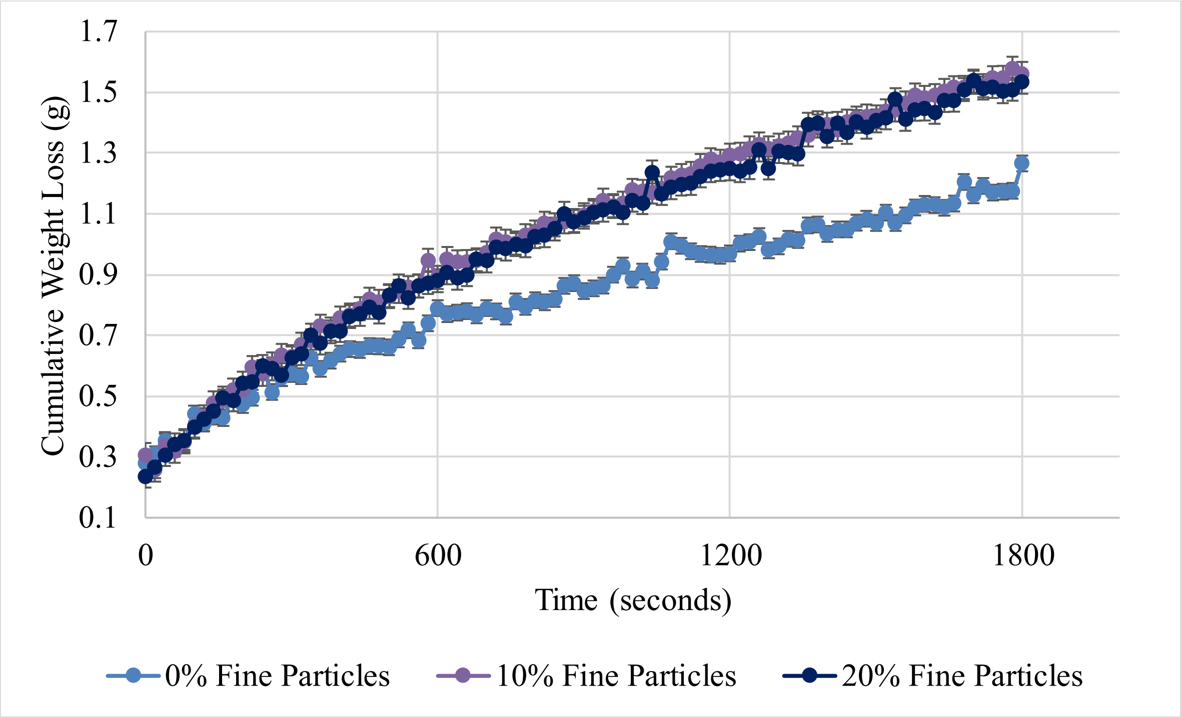

Figure 13. Drying curve for reconstituted gangue sample containing 6% water, 12% cyclohexane and different fine contents (30 minutes).

Table 7. Cyclohexane evaporated after air-drying experiment at different fine contents.

Fine Particles Content (wt. %)	Cyclohexane Evaporated (g)	Cyclohexane Evaporated (%)
0%	1.266	27.5
10%	1.562	31.8
20%	1.533	30.1

3.2.2 Microwave Experiment

The temperature of the reconstituted gangue sample was recorded every second over the duration of the microwave-drying experiment (20 minutes). Figure 14 represents a typical temperature vs time plot of a microwave-dried reconstituted gangue sample containing Soxhlet solids, water, and cyclohexane.

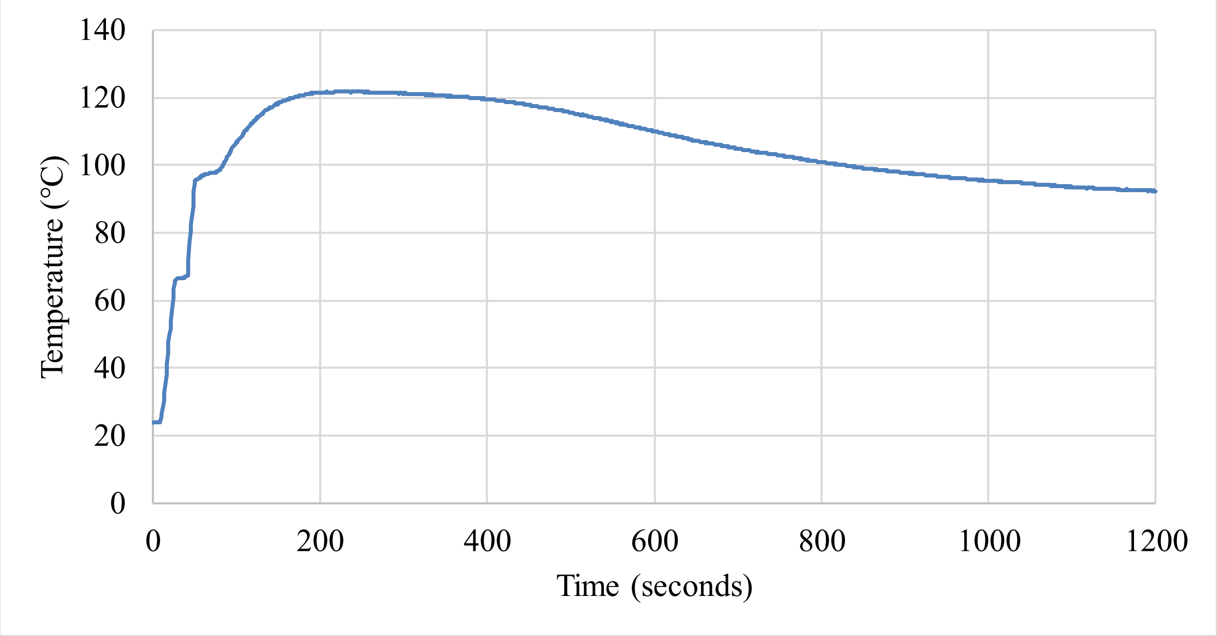

Figure 14. Typical temperature vs time plot of a reconstituted gangue sample heated using microwave.

Overall, temperature increases as long as water is present in the reconstituted gangue sample. All microwave-generated curves exhibited a similar trend with regions of little to no change in temperature in addition to regions with significant changes in temperature. Regions with no significant changes in temperature, also called plateaus, occur when the substance is going through phase change. The first plateau signifies cyclohexane boiling while the second plateau signifies water boiling. The temperature stays approximately constant while both cyclohexane and water are boiling[56]. Over the course of these segments, cyclohexane and water exist in both liquid and vapour in various ratios, starting at 100% liquid and ending at 100% vapour.

3.3 Effect of Fine Particles in microwave-only heating (Group A)

The composition of fine solids in oil sands varies with the source and quality of the oil sands. As a primary approach to investigating the effect of fine solids on solvent removal, reconstituted gangue samples of varying amounts of fines and fixed composition of fluids (cyclohexane and water) were prepared.

First, the drying behaviour of reconstituted gangue sample undergoing microwave only and containing no fines is examined. As shown in Figure 15, the heating curve follows the general trend with two distinct plateaus (regions of no significant change in temperature), in addition to regions with significant changes in temperature. The two plateaus are illustrated more evidently in Figure 16.

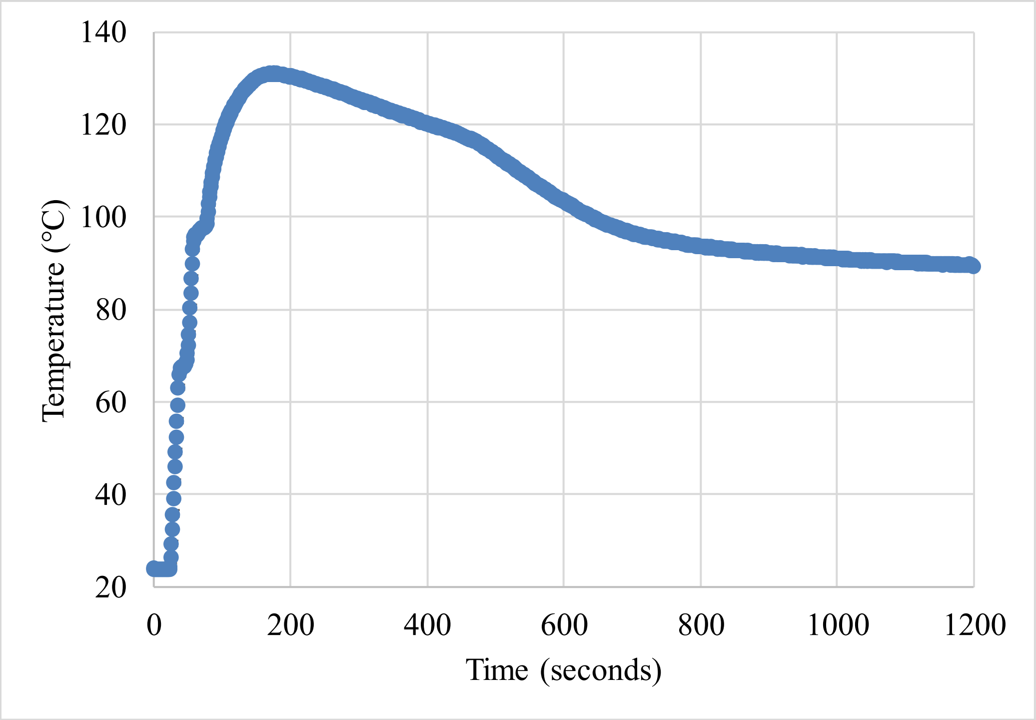

Figure 15. Temperature vs time plot of a reconstituted gangue sample containing 1 wt.% Bit. C, 6% water, 12% cyclohexane.

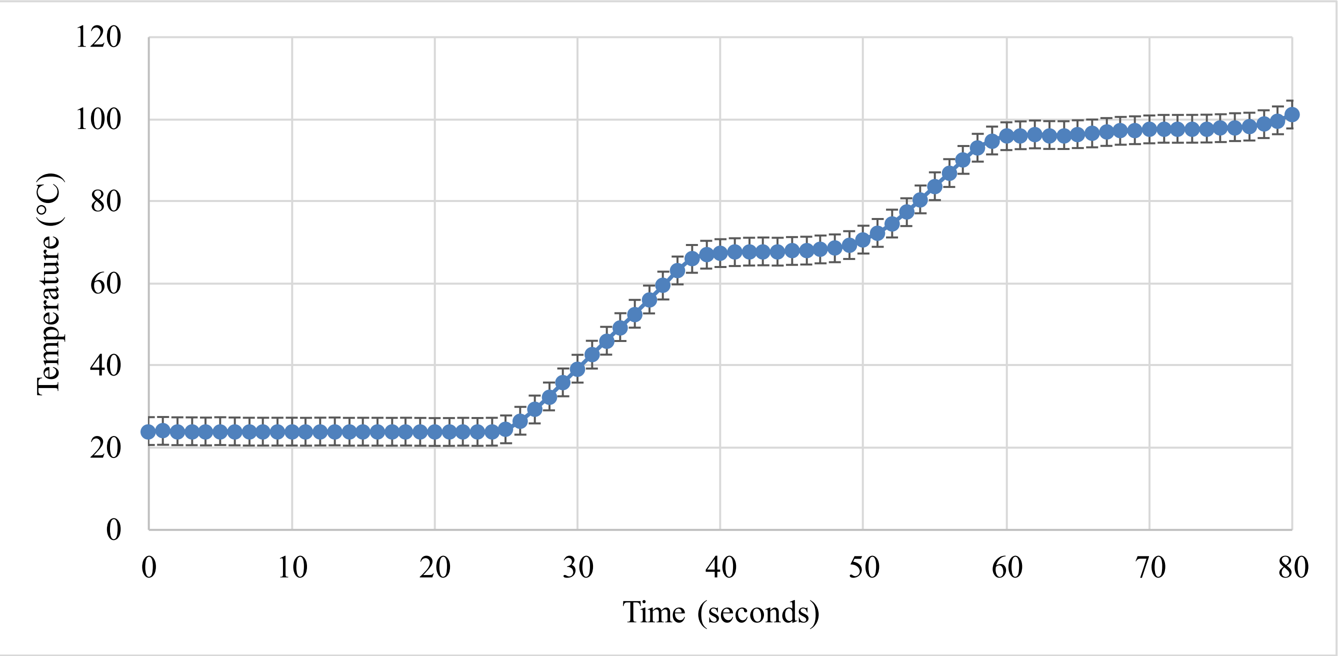

Figure 16. Plateaus of cyclohexane and water in Figure 15

The contents of the reconstituted gangue sample start to heat up after around 25 seconds. During this stage, the reconstituted gangue sample is at room temperature. After the first 25 seconds, a steady increase in temperature occurs. This steady increase is characterized by the absorption of microwave energy by water molecules, causing a significant temperature change of approximately 42°C in 13 seconds only. During the steady increase in temperature, cyclohexane is still present in liquid state and is being heated by water molecules through heat transfer after water has absorbed the bulk of the electromagnetic energy provided by the microwave.

Since energy is applied from microwave and directly to the water in the reconstituted gangue sample, the molecules of the gangue are agitated. When mixtures of immiscible liquids (cyclohexane and water in this case) are agitated, boiling occurs at a temperature lower than the boiling point of eithers components in their pure forms. This phenomenon is observed at the first plateau, which occurs at around 68 °C and remains for approximately 10 seconds. Throughout the duration of this period, cyclohexane undergoes boiling as it is being heated by water. Upon the evaporation of cyclohexane from reconstituted gangue, cyclohexane vapour is then heated along with water. Water molecules are heated with cyclohexane vapour in approximately 10 seconds, causing a temperature change of approximately 25°C as evident in the second period of steady increase in temperature.

Furthermore, the second plateau signifies the boiling of water after it has aided in the process of cyclohexane evaporation, which occurred at approximately 99 °C with a duration of around 17 seconds. At the end of the second plateau, water is present in vapour phase. The end of the second plateau indicates that water vapour, in addition to the previously evaporated cyclohexane molecules are being heated along with the rest of the components of reconstituted gangue i.e. solids. As explained previously, the major component of reconstituted gangue used in this study is the solids, which contain particles of different sizes and cover approximately 85% of the total mass of reconstituted gangue. For this reason, the maximum temperature reached by the reconstituted gangue was associated to the temperature of the solids.

In the case of 0% fines, the maximum temperature reached by the solids was 119.35°C at 207 seconds. After the peak time, the temperature of the samples dropped, indicating that the water content within the reconstituted gangue was decreasing.

Next, the drying behaviour of reconstituted gangue sample undergoing microwave only and containing 10% fine particles is examined. As shown in Figure 17, the heating curve follows the common trend with two distinct plateaus, in addition to regions with significant changes in temperature. The two plateaus are shown more clearly in Figure 18.

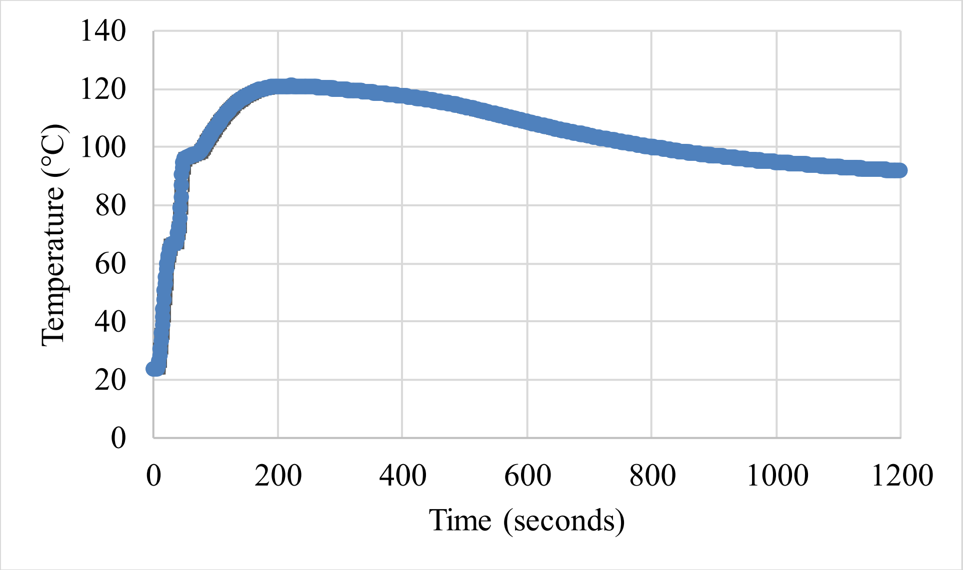

Figure 17. Temperature vs time plot of a reconstituted gangue sample containing 1 wt.% Bit. C, 6% water, 12% cyclohexane, and 10% fines.

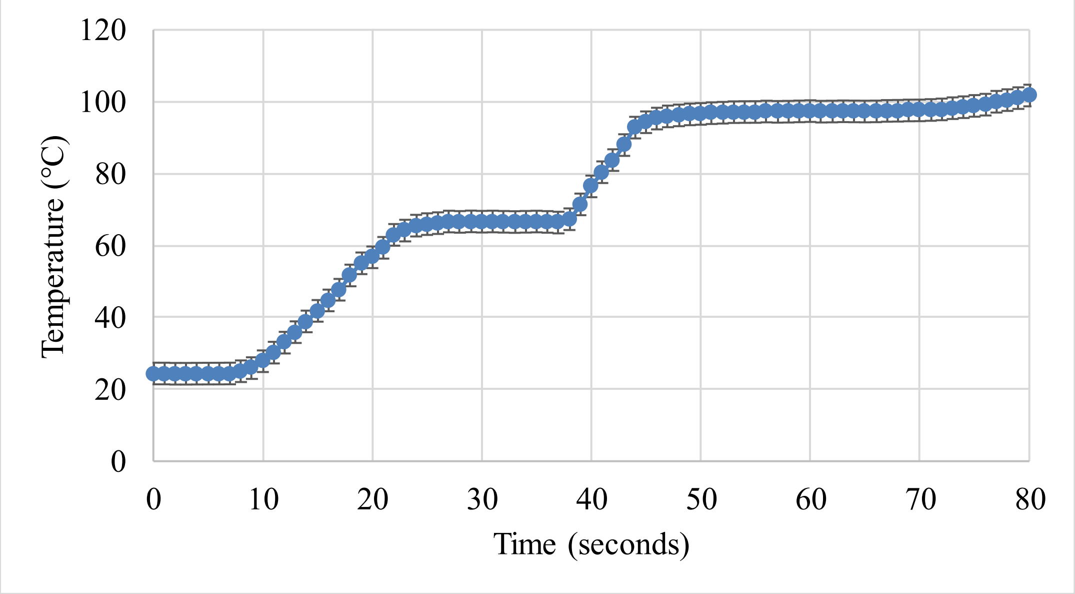

Figure 18. Plateaus of cyclohexane and water in Figure 17.

Similar to the reconstituted gangue sample with no added fine particles, after about 9 seconds, the reconstituted gangue sample's contents begin to warm up. Cyclohexane within the sample is in liquid state along with water in the beginning of the experiment. The steady increase in temperature for reconstituted gangue samples with 10% fine particles, however, required only 9 seconds to start taking place. After the first 9 seconds, the dipolar water molecules have already absorbed electromagnetic energy from microwave. Water molecules then start to heat neighboring cyclohexane molecules through heat transfer. The transfer of heat from water molecules to cyclohexane causes approximately a 35°C increase in temperature, which took place in only 13 seconds.

Cyclohexane is still present in liquid state and is being heated by water molecules through heat transfer after water has absorbed the bulk of the electromagnetic energy provided by the microwave during the period of continuous rise in temperature. When comparing the first increase in temperature in the cases of 0% and 10% fine particles, a 17% decrease occurred upon the addition of 10% fine particles to the reconstituted gangue sample. Similar to the previous case, boiling of cyclohexane occurs at a temperature lower than its normal boiling point because of the increased activity in the molecules of the gangue. The first plateau, which appears at about 67 °C and lasts for about 15 seconds, is where this phenomenon is seen.

Comparing the depressed boiling point of reconstituted gangue samples with 0% and 10% fine particles, the depressed boiling point of cyclohexane was further decreased by 1.47% when 10% fine particles were added. The duration of cyclohexane boiling (second plateau), however, increased by 50% when 10% fine particles were added. The second period of constant temperature increase indicates that in about 6 seconds, water molecules were heating cyclohexane after it has evaporated, resulting in a temperature change of about 25°C. The duration of cyclohexane evaporation in this case experienced a 40% decrease when compared to samples containing no fine particles. Furthermore, similar to the previous case, the second plateau indicates the boiling of water after it aided in cyclohexane evaporation, which took place at about 99 °C and lasted for about 27 seconds. Water is present in the vapour phase at the final point of the second plateau.

In the presence of 10% fines, the maximum temperature reached by the solids was 121°C at 221 seconds. Temperature decrease in the samples after the peak period showed that less water was present in the reconstituted gangue.

Then, the drying behaviour of reconstituted gangue sample undergoing microwave only and containing 20% fine particles is examined. As shown in Figure 19, the heating curve follows the general trend with two distinct plateaus (regions of no significant change in temperature), in addition to regions with significant changes in temperature. The two plateaus are displayed more distinctly in Figure 20.

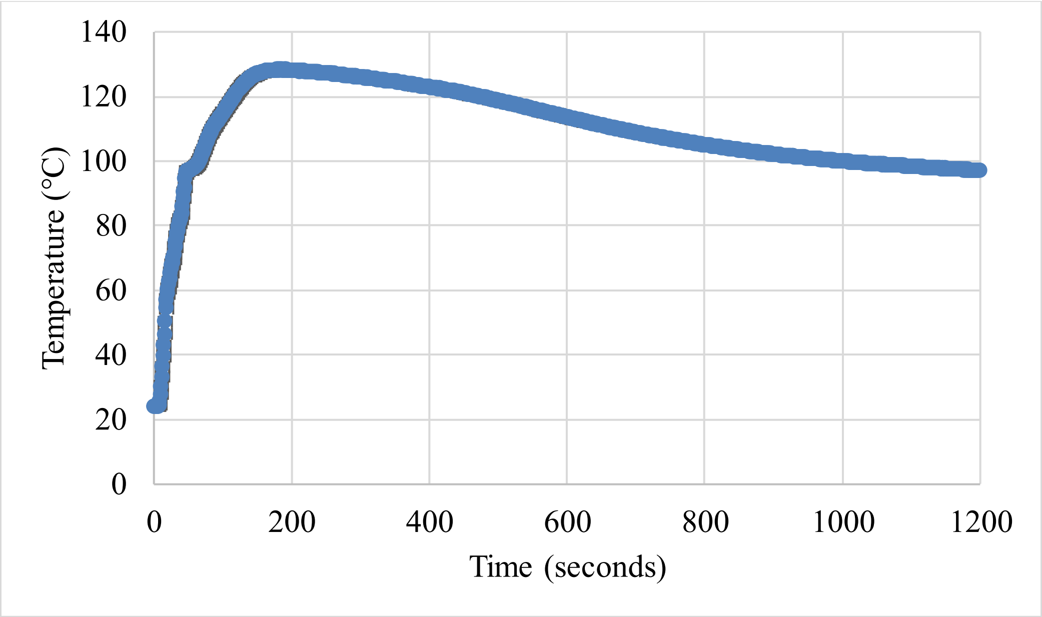

Figure 19. Temperature vs time plot of a reconstituted gangue sample containing 1 wt.% Bit. C, 6% water, 12% cyclohexane, and 20% fines.

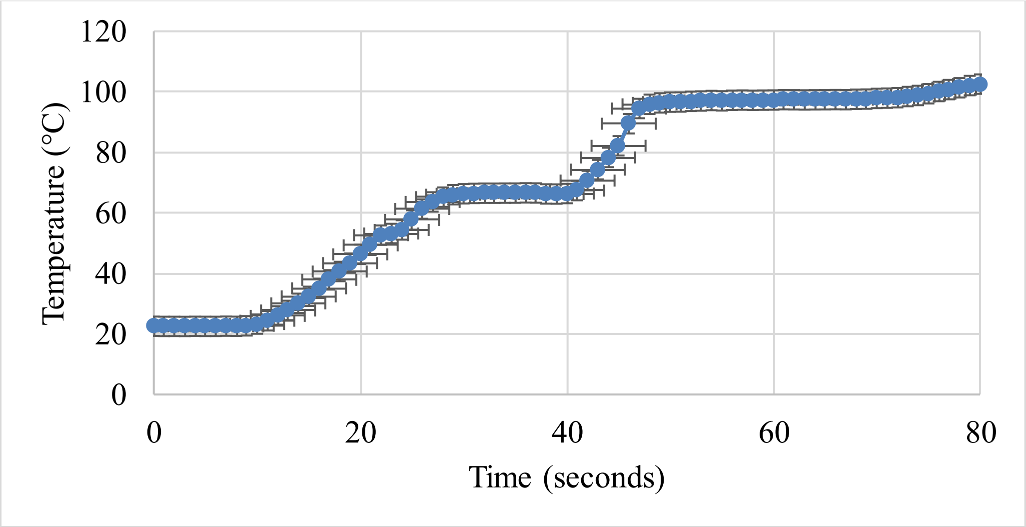

Figure 20. Plateaus of cyclohexane and water in Figure 19.

Similar to the reconstituted gangue sample with 0% and 10% added fine particles, cyclohexane within the sample is in liquid state along with water in the beginning of the experiment. However, the steady increase in temperature for reconstituted gangue samples with 20% fine particles needed only 9 seconds to start taking place. After this short period, electromagnetic energy from microwave was absorbed by water molecules, which resulted in nearby cyclohexane molecules to be heated. The transfer of heat from water molecules to cyclohexane caused approximately a 42°C increase in temperature, which took place in only 18 seconds.

When comparing the first increase in temperature in the cases of 0% and 20% fine particles, the temperature change was identical at 42°C but there was a 38.46% increase in the duration of this temperature change upon the addition of 20% fine particles to the reconstituted gangue sample. Upon the end of the steady state increase in temperature, cyclohexane starts the process of phase change, which was seen at around 66°C with a duration of 13 seconds. The temperature at which phase change occurred together with the duration exhibited 3% and 13% decrease, respectively, when compared to the case of 0% fine particles.

The second period of constant temperature increase indicates that in about 6 seconds, water molecules were heating cyclohexane after it has evaporated, resulting in a temperature change of about 27°C. The duration of this steady state period was 30% less than the case of 0% fine particles and identical to the case of 10% fine particle. The temperature change showed an 8% increase when compared to cases of 0% and 10% fine particles. Furthermore, similar to the previous cases, the second plateau took place at about 99 °C and lasted for about 27 seconds. In the case of 20% fines, the maximum temperature reached by the solids was 128.32°C at 191 seconds.

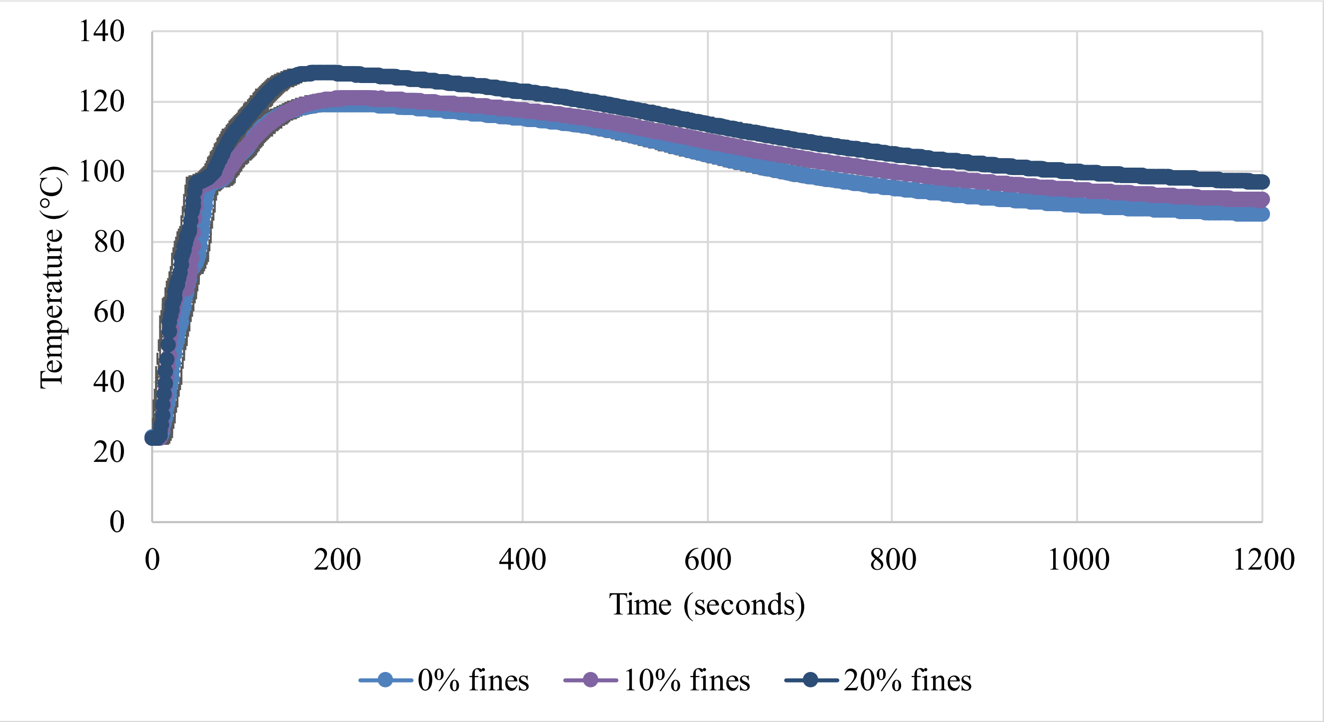

Figure 21. Temperature vs time plot of reconstituted gangue samples containing 1 wt.% Bit. C, 6% water, 12% cyclohexane, and different fine contents.

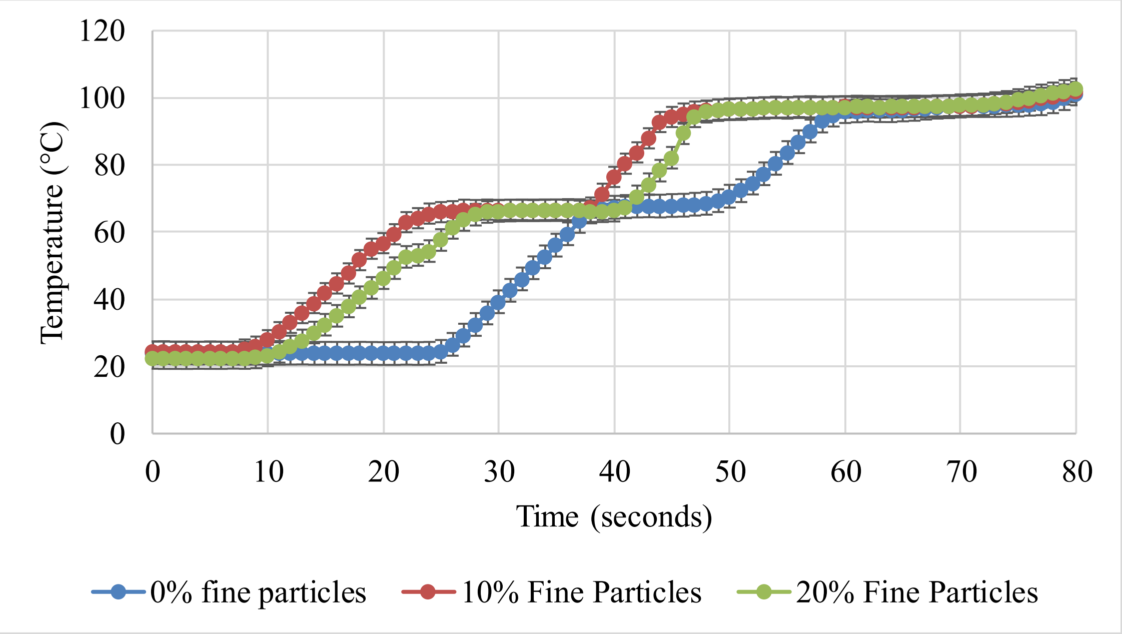

Figure 22. Plateaus of cyclohexane and water in Figure 21.

Figure 21 shows the values of reconstituted gangue samples of 1% bitumen, 6% water, 12 cyclohexane and varying amounts of fine particles. At a given time, increasing the content of fine particles wt.% decreased the boiling point of cyclohexane but had no significant change on the boiling point of water. As explained previously, the boiling of mixtures of agitated molecules occurs at a temperature lower than the boiling point of eithers components in their pure forms. This phenomenon had a significant impact on the normal boiling point of cyclohexane but appeared to have little to no influence on the normal boiling point of water. For samples with 0%, 10%, and 20% fine particles, boiling of cyclohexane occurred at 68, 67, and 66°C.

The change in boiling point for cyclohexane present in reconstituted gangue samples with varying amounts of fine particles can be explained by the two different heating mechanisms which water and cyclohexane go through. In the case of water, it is heated because of the direct interaction between the electric field of the microwave and the dipole of the water molecules. Nevertheless, heating of cyclohexane occurs through heat transfer due to the molecular collisions between the two different molecules. Initially, when the reconstituted gangue samples were free of fine particles, the time required for a temperature increase to occur at the beginning of the microwave heating experiment was approximately 25 seconds as evident in Figure 22. This duration, however, experienced a 64% decrease when 10% and 20% fine particles were added.

The significant decrease can be explained by the increase in surface area related to the addition of fine particles, recalling that fine particles are particles of sizes smaller than 45 µm. The decrease in initial temperature can be further explained by the fact that upon the addition of small fine particles, water molecules are exposed to more surface area. The increased content of hydrophilic fine particles resulted in the decrease of the initial time required to heat the reconstituted gangue samples. The period at which cyclohexane underwent phase change (length of first plateau) was increased by 50% and 30% upon the addition of 10% and 20% fine particles, respectively, when compared to samples with no added fines.

This can be explained by the increased surface area offered by samples containing fine particles. Water molecules in reconstituted gangue samples with fine particles had a larger surface area to heat when compared to reconstituted gangue samples with 0% fine particles. This larger surface area demanded more time to be heated, which resulted in the increase in the duration of cyclohexane phase change (first plateau) in samples containing fine particles. Unexpectedly, the period at which cyclohexane underwent phase change reached its maximum at 10% fine particles content.

Moreover, surface area can also be related to the 40% reduction during the second period of constant temperature increase (cyclohexane evaporation) in samples with 10% fines. An increased surface area means that more particles are exposed to the heating agent (water), which decreases the time required to evaporate the solvent. However, when comparing cyclohexane evaporation in samples with 10% and 20% fine particles, there was no significant change. At higher fine particles content, the time required to evaporate cyclohexane from reconstituted gangue samples becomes independent on fine particles content. As evident in the experimental results, a critical fine particles content from which cyclohexane evaporation is no longer dependent on fine particles content can be seen.

At the critical content of fine particles, higher fines content cannot further reduce the time required to evaporate cyclohexane from the reconstituted gangue. Apparently, for any microwave-heated gangue samples with 1% wt. bitumen and 12% wt. cyclohexane, the amount of time it takes cyclohexane to evaporate from the gangue is dependent on the content of fine particles, provided that the fine particles are present in amounts of 10% wt. or below, based on weight of Soxhlet solids.

3.3.1 Average Maximum Temperature

The solids, which contain particles of various sizes and make up around 85% of the overall mass of the reconstituted gangue, are the main component used in this study. Because of this, the temperature of the solids and the maximum temperature reached during microwave heating were related.

Upon the heating of reconstituted gangue samples, the temperature of the solids reached maximum levels then started to decrease till the end of the experiment. In Figure 23, The average maximum temperature was correlated to the fine particles content to investigate the relationship between the maximum temperature reached by Soxhlet solids containing fine particles and the fine particles content.

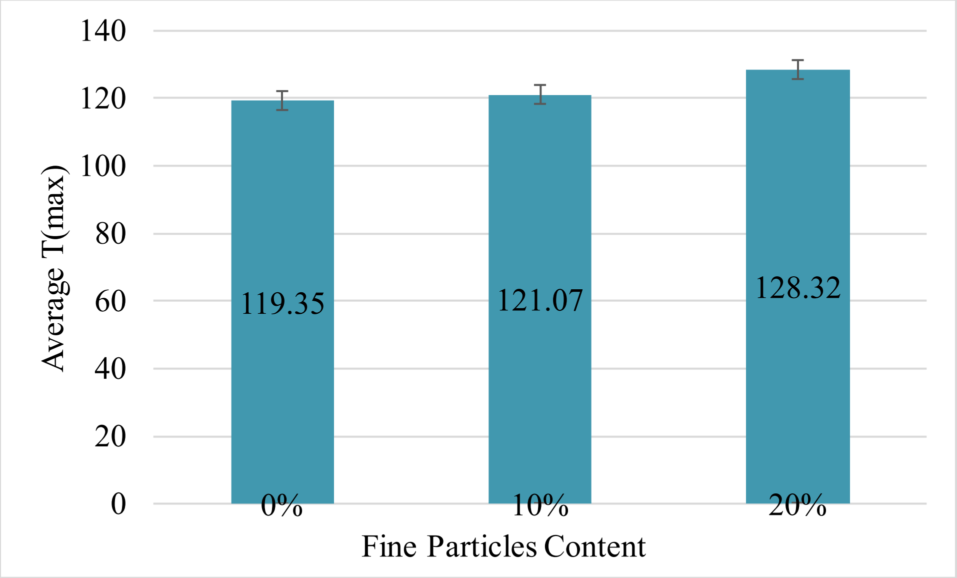

Figure 23. Average maximum temperature vs fine particles content.

The presence of fine particles at an amount of 10% based on weight of Soxhlet solids increased the maximum temperature from 119.35 °C to 121.07 °C when compared to Soxhlet solids containing no fine particles. When comparing the percentage increase of maximum temperatures of reconstituted gangue samples with 10% and 20% fine particles, there was approximately a 6% increase in maximum temperature. The maximum temperature reached by reconstituted gangue samples with 20% fine particles had an increase of 7.52% when compared to Soxhlet solids containing no fine particles. It can be assumed that the change in maximum temperature of reconstituted gangue samples with fine contents up to 10% is negligible, whereas change in maximum temperature of solids containing more than 10% fine particles is considerable. Figure 24 represents how the average maximum temperature is correlated to the fine particles content using a polynomial of second degree.

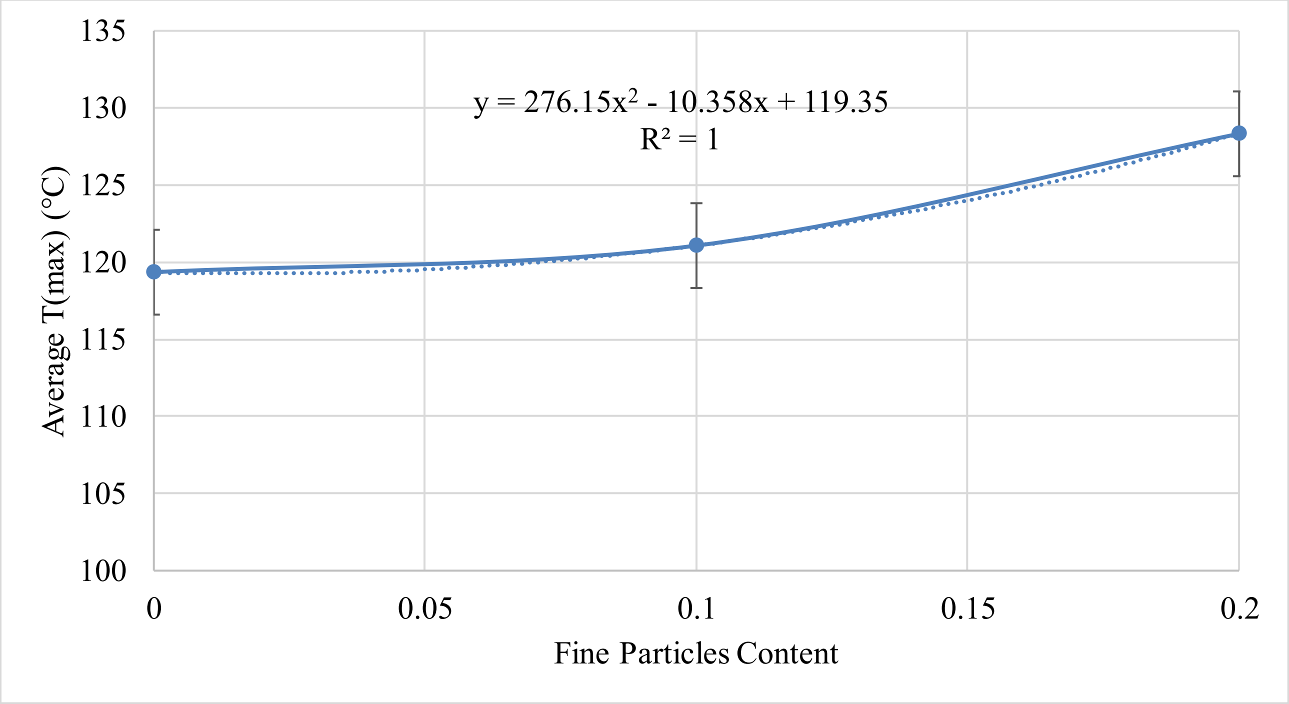

Figure 24. Plot of average maximum temperature reached by solids vs fine particles content.

3.3.2 Residual Cyclohexane

Table 8. Average values of residual cyclohexane in the gangue.

Fine Solids Content (wt.%)	Average residual cyclohexane (ppm)
0%	493±233
10%	517±335
20%	773±184

It is clear from Table 8 that the average residual cyclohexane content is directly correlated to the fine solids content, as seen by the increase in residual cyclohexane concentration when the fine solids content was increased. As explained previously, the removal of cyclohexane from microwave-heated reconstituted gangue samples is accomplished due to heat transfer between water and cyclohexane. The presence of water is therefore critical to cyclohexane removal during microwave heating. The final stage in air-drying experiments was cooperatively characterized by water evaporation[29-32], where cyclohexane removal is limited by diffusion within the gangue. This is also the case in microwave heating as seen from the second plateau where water goes through phase change before evaporation.

Furthermore, the drop in temperature after the maximum temperature was reached indicated that the content of water and cyclohexane present in the gangue were decreasing. At this point, there is residual cyclohexane that is retained in the pores of the gangue that are vacant as water evaporates. Since water acts as the heating medium in microwave heating, the remaining cyclohexane will be difficult to remove when there is no water left in the gangue. Nevertheless, microwave heating was sufficient for the removal of more than 99% of cyclohexane present in the reconstituted gangue.

3.4 Effect of Fine Particles in Air-Drying Followed by Microwave Heating (Group B)

Similar to reconstituted gangue samples in section 3.3, the temperature of the samples was recorded every second for 20 minutes. Figure 25 represents a typical temperature vs time plot of a reconstituted gangue sample which was air-dried prior to being heated by microwave. Generally, all samples that underwent air-drying prior to microwave heating demonstrated both cyclohexane and water plateaus. Nevertheless, cyclohexane plateaus in Group B were unnoticeable when compared to those in Group A.

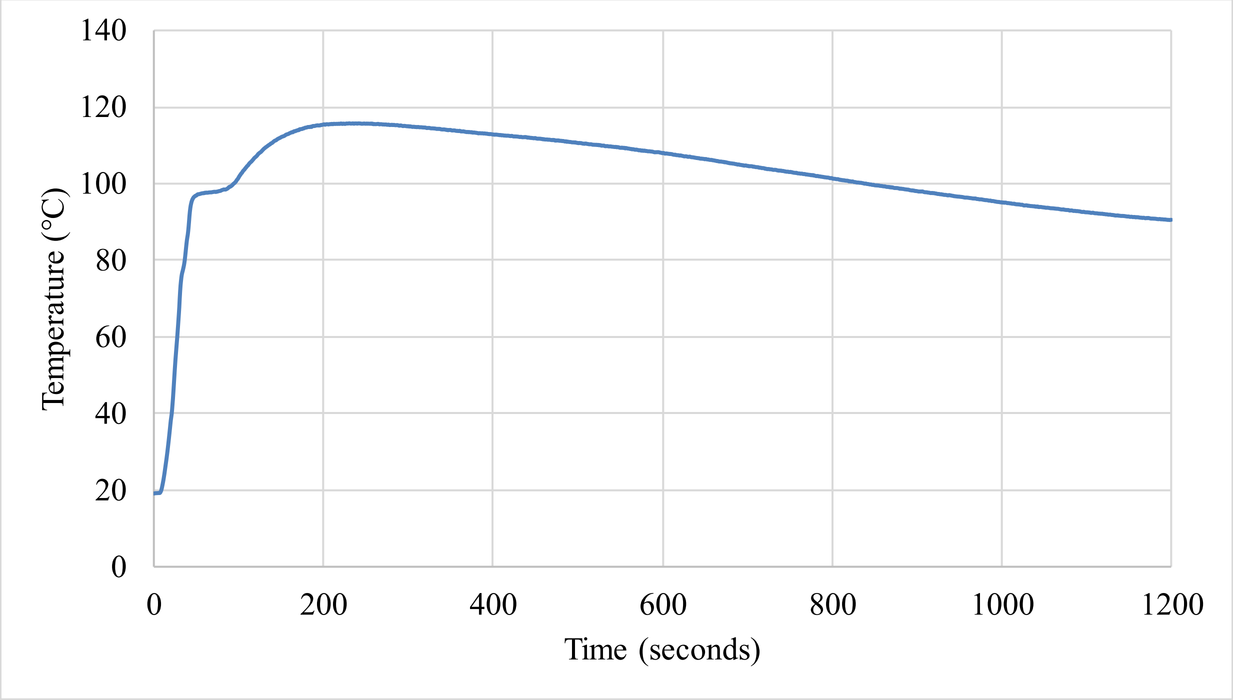

Figure 25. Typical temperature vs time plot of a reconstituted gangue sample dried using air-drying followed by microwave.

Figure 26 shows the average temperature vs. time plot of reconstituted gangue samples with 0 wt.% fine particles. The heating curve follows the general trend with water plateau being more evident than cyclohexane plateau. Figure 27 shows the two plateaus.

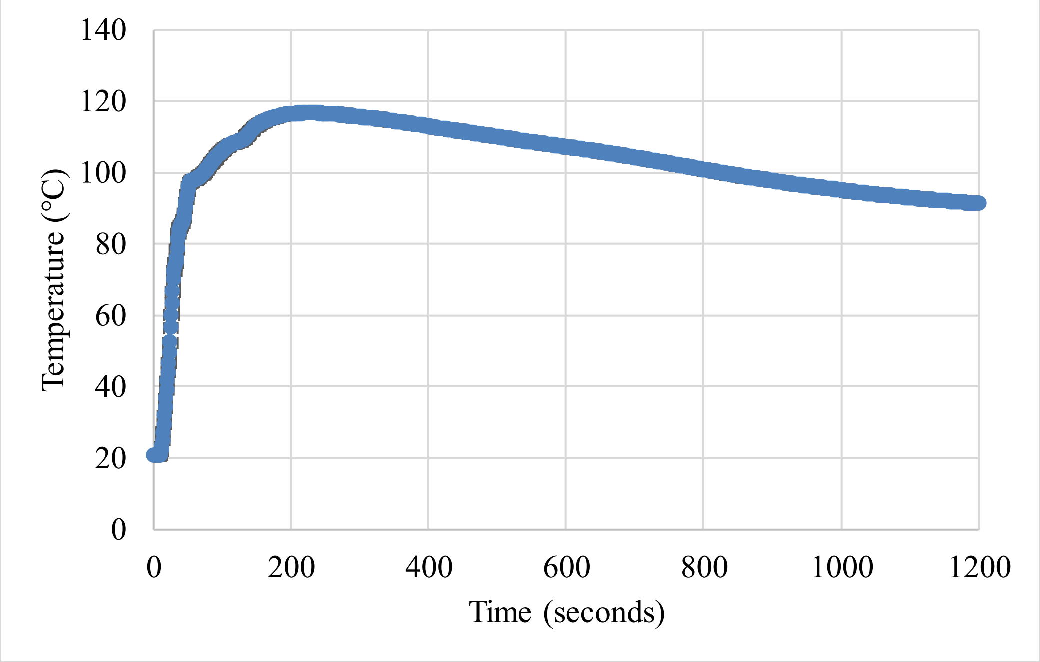

Figure 26. Average temperature vs time plot of a reconstituted gangue sample containing 1 wt.% Bit. C, 6% water, 12% cyclohexane.

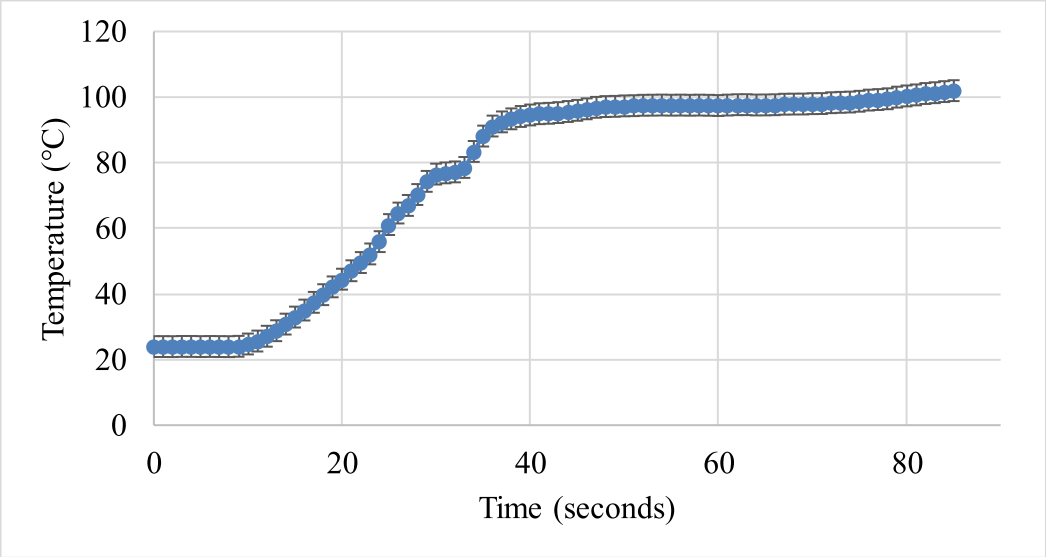

Figure 27. Plateaus of cyclohexane and water in Figure 26.

About 10 seconds passed before the contents of the reconstituted gangue begin to heat up. The reconstituted gangue sample was at room temperature before the temperature started to increase steadily after only 10 seconds. Similar to previous microwave-heated reconstituted gangue samples, this gradual increase in temperature is due to water molecules absorbing microwave energy, which resulted in a large temperature change of about 52°C in just 20 seconds. Cyclohexane, which is still present in liquid state, starts to boil after the first 30 seconds as seen from the first plateau in Figure 27. Boiling of cyclohexane becomes evident at around 77.5 °C as the solvent is heated by neighboring water molecules which absorbed the bulk of microwave energy.

Furthermore, when reconstituted gangue samples are subjected to air-drying prior to microwave-heating, boiling of cyclohexane occurs at a temperature close to its normal boiling point. For reconstituted gangue samples dried using only microwave (Group A), cyclohexane was present in substantial amounts, causing an increase in the activity of molecules when heated by water. This increase in activity caused an apparent depression in the normal boiling point of cyclohexane, which was not as apparent for gangue samples dried using air-drying followed by microwave (Group B).

Moreover, cyclohexane undergoes boiling for 3 seconds before it starts to evaporate from the reconstituted gangue sample. Subsequently, the duration of cyclohexane evaporation was 3 seconds and caused approximately a 13°C increase in temperature. The maximum temperature reached by the solids in the case of 0% fine particles was 116.71°C at 207 seconds.

When comparing samples containing 0% fine particles in Groups A&B, there appeared to be a 60% decrease in the time required to heat the gangue at the start of the microwave experiment, which was in favour of samples undergoing air-drying prior to microwave heating. The duration of cyclohexane boiling and evaporation in samples with no added fine particles experienced a 70% decrease when air-dried prior to microwave heating. The temperature change during cyclohexane evaporation decreased by 48% when gangue samples containing no added fine particles were air-dried before microwave heating.

Next, Figure 28 shows the average temperature vs. time plot of reconstituted gangue samples containing 10 wt.% fine particles with cyclohexane and water plateaus illustrated more distinctly in Figure 29.

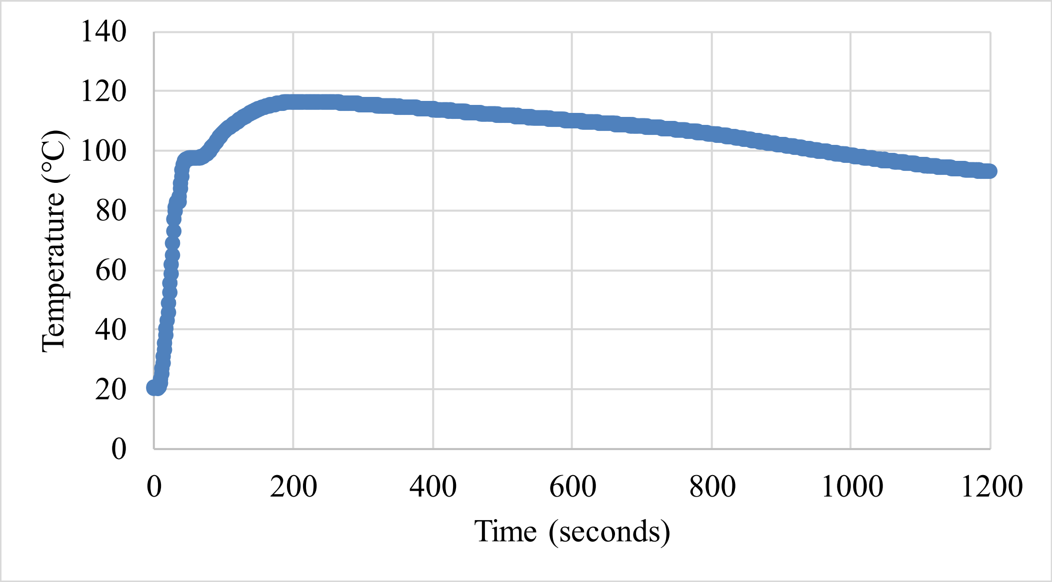

Figure 28. Average temperature vs time plot of a reconstituted gangue sample containing 1 wt.% Bit. C, 6% water, 12% cyclohexane, and 10% fines.

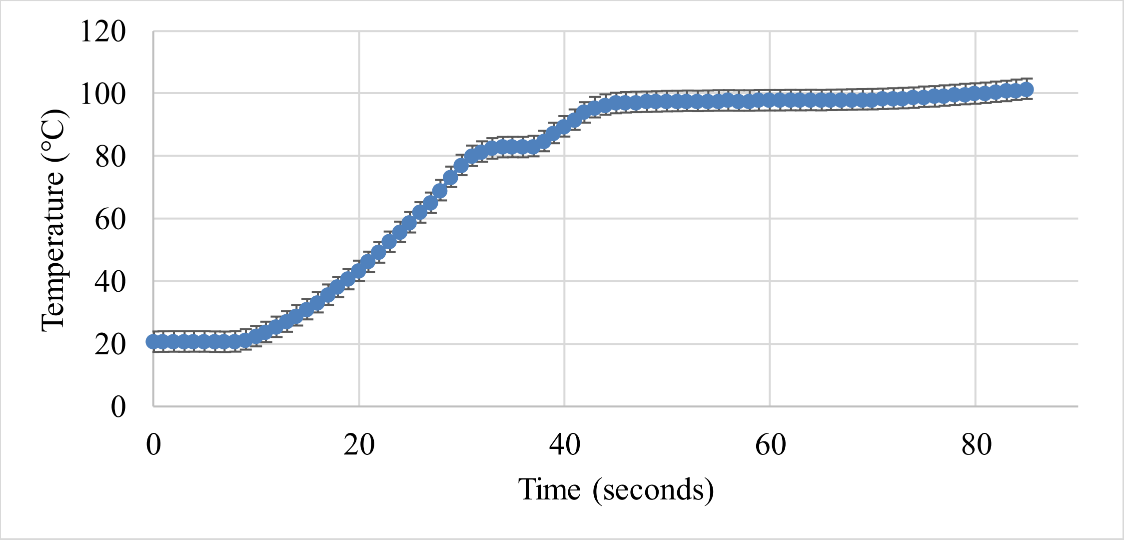

Figure 29. Plateaus of cyclohexane and water in Figure 28.

Upon the addition of 10 wt.% fine particles, the reconstituted gangue sample started to heat in about 8 seconds. Afterwards, in just 23 seconds, temperature increased by about 59°C as a result of heat being transferred from water molecules to cyclohexane. Liquid cyclohexane is being heated by water molecules and begins to boil at approximately 82°C, a temperature close to its normal boiling point. Time required to initially heat reconstituted gangue sample fell by 20% when 10% fine particles were added to the reconstituted gangue sample, whereas the first increase in temperature increased by 15%.

The duration of cyclohexane boiling has more than doubled relative to samples containing 0% fine particles. Water molecules were heating cyclohexane after it has evaporated as evident in the second period of constant temperature increase, which was 6 seconds long and resulted in a temperature change of around 12°C. Cyclohexane required double the time to evaporate from reconstituted gangue samples upon the addition of 10% fine particles. Moreover, unlike samples which were only microwaved, cyclohexane in samples undergoing air-drying before microwave boils at a temperature close to its normal boiling point.The depression in normal boiling point was not as evident for samples in Group B because air-drying aided in the process of removing a significant amount of cyclohexane, thus, decreasing the activity of the molecules of the gangue.

In the presence of 10% fines, the maximum temperature reached by the solids was 116.82°C at 225 seconds. Less water and cyclohexane were present in the reconstituted gangue after the maximum temperature, as evidenced by a drop in temperature.

Then, the average temperature vs. time plot of reconstituted gangue samples with 20% fine particles is also shown in Figure 30, with the regions of cyclohexane and water evaporation being shown more clearly in Figure 31.

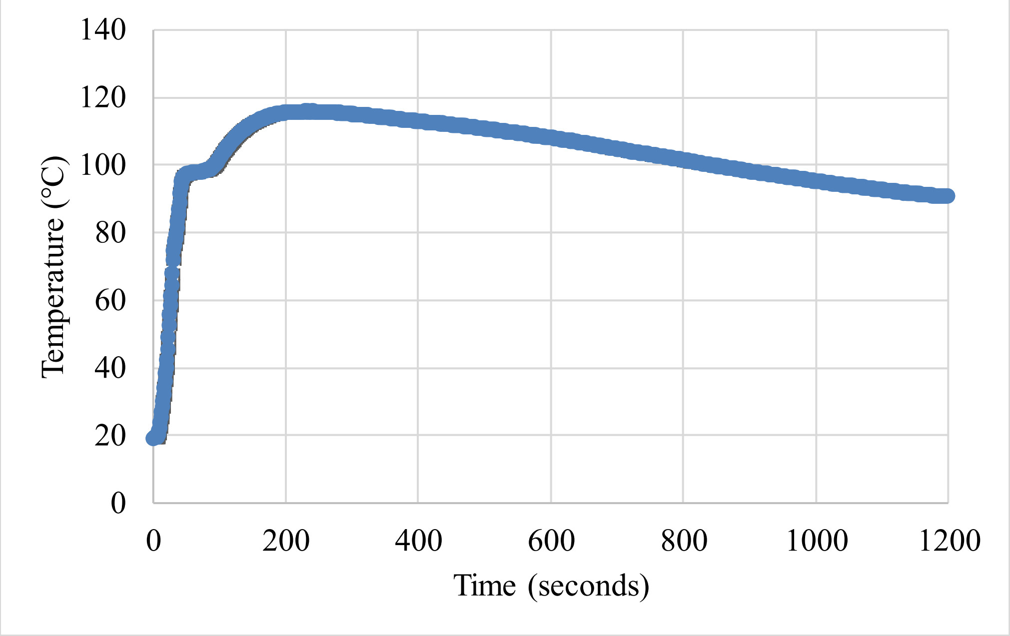

Figure 30. Average temperature vs time plot of a reconstituted gangue sample containing 1 wt.% Bit. C, 6% water, 12% cyclohexane, and 20% fines.

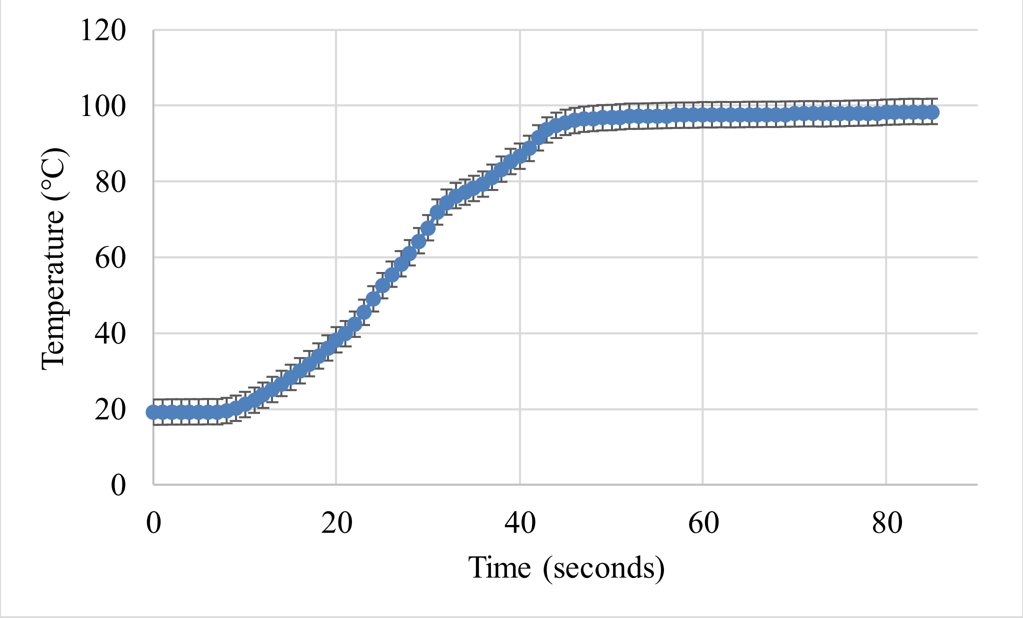

Figure 31. Plateaus of cyclohexane and water in Figure 30.

The reconstituted gangue sample began to heat with the addition of 20% fine particles in around 7 seconds. The temperature then rose by around 57°C in just 26 seconds before cyclohexane started to boil. The presence of 20% fine particles in the reconstituted gangue sample decreased the initial heating time by 30% and 12.5% when compared to samples with 0% and 10% fine particles, respectively. Temperature increased by about 57°C in just 26 seconds before cyclohexane started to boil.

In samples containing 0%, 10%, and 20% of fine particles discussed previously, the length of the first plateaus, which was the time required for cyclohexane to go through phase transition, were approximately horizontal. This was not the case for samples containing 20% fine particles which underwent air-drying prior to microwave heating, as evident in Figure 31. The region of phase change in these samples is not as evident, and cyclohexane is observed to change phase for approximately 3 seconds, before it starts to evaporate steadily as soon as it approaches its normal boiling point. The increased surface area provided by samples with 20% fine particles along with pre-drying at ambient conditions can be used to explain this.

In comparison to reconstituted gangue samples with 0% and 10% fine particles, cyclohexane in gangue samples with 20% fine particles was spread out on a larger surface area to heat. Cyclohexane evaporates more quickly the more surface area it occupies. After the Soxhlet solids had reached a maximum temperature of 115.74°C at 230 seconds, the temperature decreased, indicating the presence of less water and cyclohexane.

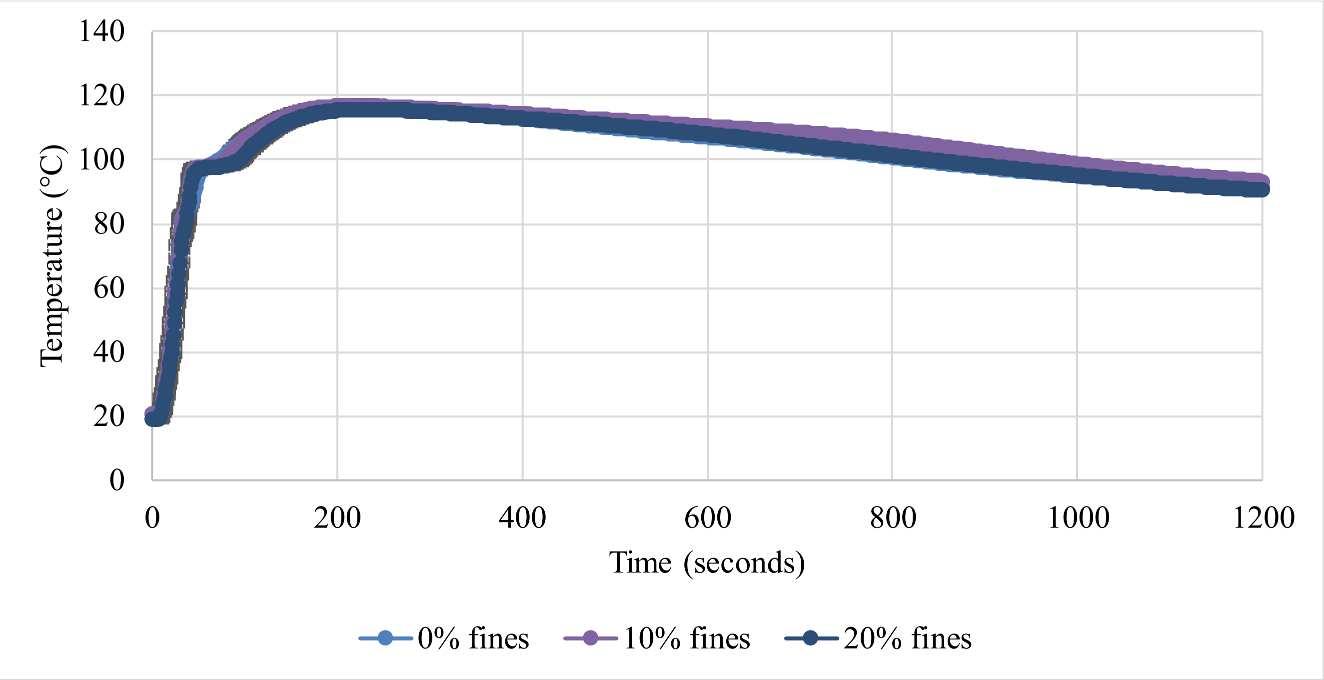

Figure 32. Average temperature vs time plots of reconstituted gangue samples containing 1 wt.% Bit. C, 6% water, 12% cyclohexane, and different fine contents.

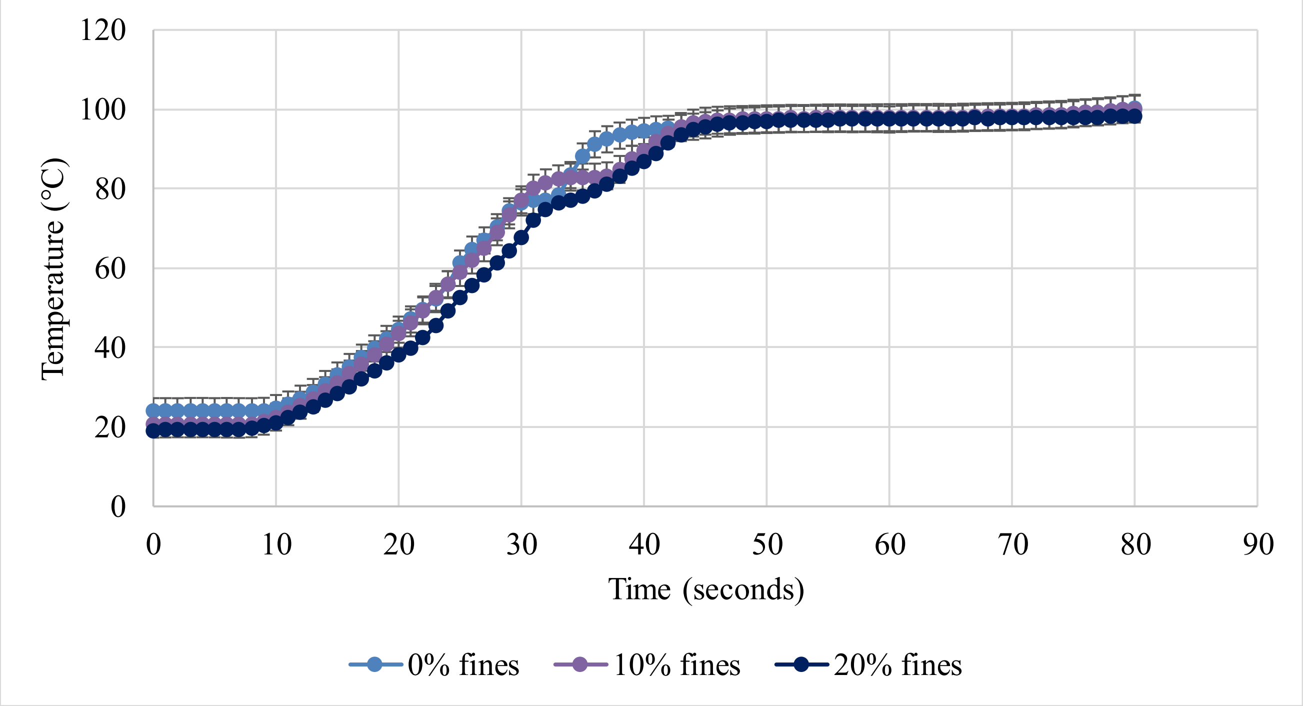

Figure 33. Plateaus of cyclohexane and water.

The average results of reconstituted gangue samples with 1% bitumen, 6% water, 12% cyclohexane, and different amounts of fine particles are shown in Figure 32. When the fine particles content was 10%, the boiling point of cyclohexane was slightly more than its normal boiling point. For samples with 0% and 20% fine particles, the boiling point of cyclohexane was slightly less than its normal boiling point. This was not the case for the boiling point of water as clear from the water plateau in Figure 33 which occurred at around 100°C for all three percentages of fine particles.

When comparing samples with 0% and 10% fine particles, the period at which cyclohexane underwent phase change was more than doubled upon the increase in fines content. In addition, cyclohexane required double the time to evaporate from reconstituted gangue samples with 10% fine particles. This can be explained by the increased surface area offered by samples with 10% fine particles. For reconstituted gangue samples containing 20% fine particles, boiling of cyclohexane was comparable to reconstituted gangue samples containing no fine particles.

For samples in Group B, there appears to be a fine particles content where the duration of cyclohexane boiling reaches its maximum. Moreover, the time required to evaporate cyclohexane from the gangue was doubled for samples containing 10% fine particles and tripled for samples containing 20% fine particles relative to samples containing no fines. The presence of fine particles dramatically increased the time required to evaporate cyclohexane from reconstituted gangue samples.

3.4.1 Average Maximum Temperature

As explained in Section 2.1, the mass of reconstituted gangue samples contains mostly Soxhlet solids, which is the main component used in this study. As a result, there was a correlation between the temperature of the solids and the highest temperature obtained during microwave heating. Figure 34 shows a bar chart of the relationship between the maximum temperature achieved during microwave heating and the fine particles content in the gangue samples.

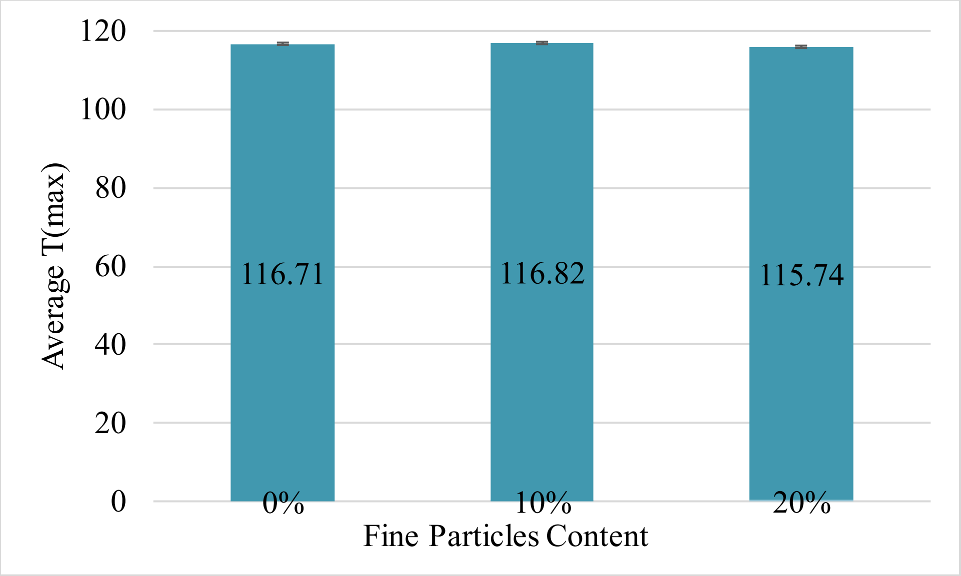

Figure 34. Average maximum temperature vs fine particles content.

In comparison to Soxhlet solids without fine particles, the presence of fine particles at an amount of 10% based on weight of Soxhlet solids increased the maximum temperature from 116.71 to 116.82. In contrast, when comparing the percentage decrease of maximum temperatures of reconstituted gangue samples with 10% and 20% fine particles, there was approximately a 1 °C decrease in the maximum temperature. The maximum temperature reached by reconstituted gangue samples with 20% fine particles had a decrease of 1 °C when compared to reconstituted gangue samples containing no fine particles. Although the changes in maximum temperature reached by the reconstituted gangue samples undergoing air-drying before microwave heating were negligible, it can be predicted that reconstituted gangue samples with fine contents up to 20% will experience no significant change in maximum temperature. Figure 35 shows the relationship between the fine particles content and the average maximum temperature when a polynomial of second degree is used.

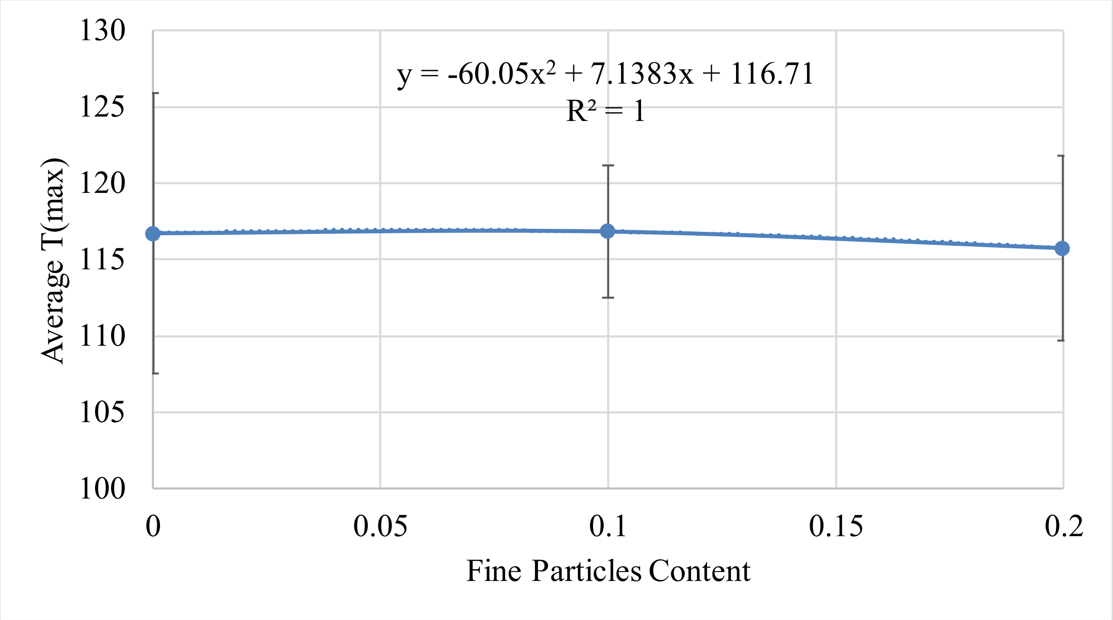

Figure 35. Plot of average maximum temperature reached by solids vs fine particles content.

3.4.2 Residual Cyclohexane

Table 9. Average values of residual cyclohexane in the gangue.

Fine Solids Content (wt.%)	**Average residual cyclohexane (ppm)**
0%:	127±111
10%	148±68
20%	120±26

Table 9 shows that the average residual cyclohexane content is comparable for reconstituted gangue samples containing up to 20 wt.% fine particles. The highest amount of residual cyclohexane was detected at 10 wt.% fine particles content. This fine particle content was also linked to have the maximum duration of cyclohexane phase change in Group B when compared to 0 wt.% and 20 wt.% fines contents. This duration, however, was comparable for samples containing 0 wt.% and 20 wt.% fine particles, which is also the case for residual cyclohexane.

Although cyclohexane goes through phase change and evaporates during microwave heating, cyclohexane vapours can get trapped in the tiny pores of the gangue in the absence of water. Residual cyclohexane will be challenging to remove without water during microwave heating. At increased contents of fine particles, however, there exists a fine particles content (10 wt.%) where boiling of cyclohexane during microwave heating in addition to residual cyclohexane content are maximized. Interestingly, this observation was only attributed to reconstituted gangue samples undergoing air-drying prior to microwave heating.

Regardless of the residual cyclohexane content, microwave heating was successful in the removal of more than 99% of the cyclohexane present in the reconstituted gangue in both cyclohexane removal processes.

4. Conclusions

This research investigated the effect of varying the content of fine particles (0%, 10%, 20%) at constant bitumen (1 wt.%), water (6 wt.%), and cyclohexane (12 wt.%) contents on the removal of cyclohexane from reconstituted gangue samples using two different solvent removal mechanisms: microwave-only and air-drying followed by microwave. Dean-Stark extraction was used to separate the oil sands components and obtain Soxhlet solids, which was the primary component used for the preparation of reconstituted gangue that contained fine particles. The reconstituted gangues were crucial because they provided a controlled sample whose composition could be modified depending on the variable to be investigated. Reconstituted gangue samples were then prepared with fixed amounts of bitumen, water, cyclohexane, and different contents of fine particles.

In comparison to air-drying, microwave heating is regarded as a selective process with significant advantages. This heating method transfers energy directly to materials that absorb microwaves and compares advantageously in terms of the rate and amount of cyclohexane removed. The removal process depends on the fact that the normal boiling point of cyclohexane is lower than that of water and that cyclohexane is removed before water.

For samples undergoing only microwave heating (Group A), the temperature of the reconstituted gangue samples was recorded every second for 20 minutes. A typical temperature vs. time plot of a reconstituted gangue sample heated through microwave is characterised by areas with little to no change in temperature as well as areas with noticeable variations in temperature. When a substance is undergoing a phase change, areas with minimal temperature changes—also known as plateaus—occur. The first plateau denotes the boiling of cyclohexane, whereas the second plateau denotes the boiling of water.

For samples undergoing air-drying followed by microwave heating (Group B), all samples were dried under a fume hood for 30 minutes at ambient conditions and the weight was continuously logged before being heated in a microwave oven. Collectively, air-drying experiments in the past have shown that a substantial evaporation flux occurs during the first stages of the drying experiment. The presence of liquid cyclohexane films and their connection to the exposed surface of the reconstituted gangue provide an explanation for this. Cyclohexane evaporation was noticed to decrease towards the end of the air-drying experiment due to the decrease in liquid film connection inside the reconstituted gangue, indicating the need for greater energy input to remove the cyclohexane remaining in the gangue. For this reason, samples were heated in a microwave following the end of the air-drying experiment to accelerate the final stage of cyclohexane evaporation.

Moreover, the initial heating time for the reconstituted gangue samples was reduced in both solvent removal mechanisms because of the increased amount of hydrophilic fine particles. The time needed for cyclohexane to transition from the liquid to gas phase reached a maximum at 10% fine particles for both solvent removal mechanisms. Relative to samples containing no fine particles, the average maximum temperature of reconstituted gangue was approximately constant for samples with 10 wt. % fine particles, whereas samples containing 20% fine particles had a considerable change in the average maximum temperature, regardless of the solvent removal mechanism used.

Cyclohexane in gangue samples undergoing only microwave heating required more time to go through phase change when compared to samples undergoing air-drying prior to microwave heating, regardless of fine particles content. In addition, the temperature at which cyclohexane underwent phase change was significantly depressed for all samples undergoing microwave heating for all contents of fine particles. There was no noticeable difference between the duration of cyclohexane evaporation in samples with 10% and 20% fine particles when the solvent removal mechanism used was only microwave. At increased contents of fine particles, the time required for cyclohexane to be removed from the gangue becomes independent on fine particles content. The maximum temperature reached by the Soxhlet solids remained unchanged for gangue samples with fine particles up to 10 wt.% but increased upon the addition of 20 wt.% fine particles, relative to samples containing 0 wt.% fine particles.

For samples in Group B, the duration at which cyclohexane underwent phase change reached its maximum at 10 wt.% fine particles content. This duration, however, was comparable for samples containing 0 wt.% and 20 wt.% fine particles. The temperature at which cyclohexane underwent phase change was comparable to cyclohexane's normal boiling point for all contents of fine particles. The duration of cyclohexane evaporation in gangue samples containing 10% and 20% fine particles was doubled and tripled, respectively, in comparison to gangue samples containing no fine particles. At increased contents of fine particles, the time required for cyclohexane to evaporate from the gangue significantly increases. The average maximum temperature reached by the Soxhlet solids was approximately constant for all contents of fine particles, indicating that the temperature reached by Soxhlet solids is independent on the content of fine particles when the gangue is air-dried prior to microwave heating.

4.1 Future Recommendations

This research demonstrated that microwave heating can be utilised to remove cyclohexane from the gangue and provided insight on the effect of fine particles on the heating process. Nevertheless, more research is required to understand the role of other important parameters, such as bitumen, water, and cyclohexane in microwave heating. Compositional parameters of the gangue should be controlled and studied in order to achieve more efficient drying. Residual bitumen has been proved by numerous researchers to be detrimental in the process of solvent removal from the gangue using an air-drying method. For this reason, it is recommended to focus on further improving the extraction performance in NAE methods. The role of residual bitumen and water in solvent removal using microwave heating is yet to be known. Investigating the major parameters that control the drying process of the gangue is a vital part of the drying process.

If non-aqueous extraction technique is to be commercialised with cyclohexane as a solvent, the gangue obtained after the extraction must be dried immediately because of the toxic solvent. Additionally, a thorough study of the safety aspects is required prior to commercialisation. While cyclohexane is manufactured by catalytic hydrogenation of benzene and unreacted benzene can be found in cyclohexane as an impurity, the grade of cyclohexane used in the extraction must be free from impurities[57]. Exposure to benzene can lead to serious health effects and its removal from cyclohexane is crucial.

In this research, the prepared reconstituted gangue samples were examined in small amounts (25 g of gangue with a sample thickness of 1 cm for air-drying and 5 grams with height of 1.5 cm for microwave heating). However, the volume of gangue that would result from commercialization would be substantially higher. These differences must be taken into consideration because any scale-up can possibly alter the effect of specific components. Bed height in air-drying experiments was demonstrated in [29] to affect the final residual cyclohexane content in the gangue. Reducing the bed height can be advantageous since it greatly reduces the amount of residual cyclohexane. If the second solvent removal mechanism (air-drying prior to microwave heating) were to be used in industry, large spaces will be required to spread out and pack the extracted gangue prior to microwave heating. Economical and energy analysis of microwave technology must also be considered in order to find the cost of the solvent removal process.

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