Microwave Heating of Non-Aqueous Oil Sands Extraction Gangue: Study of Optimal Cyclohexane-Water Mass Ratio and Solvent Recovery Rate

by

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A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science

in

Chemical Engineering

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Abstract

Non-aqueous bitumen extraction processes (NAE) of mined oil sands ore have been investigated to circumvent the environmental and operating limitations of the current hot water-based technology. However, one primary challenge of NAE is a solvent recovery that meets environmental and economic constraints. Microwave heating (MWH) has been identified as a possible solution due to its selective and rapid heating nature. Nonetheless, this technology is still in the early stages of development, requiring a better understanding of concentrations of solvent and fines that are industrially relevant. Therefore, this work quantifies the solvent removal (cyclohexane) from NAE reconstituted gangue using MWH across different concentrations of cyclohexane, fines particles, and water (MWH absorber). Based on the previous literature, two main mechanisms are suggested for the solvent removal from NAE reconstituted gangue. The main mechanism is attributed to the selective heating of water that efficiently transfers energy to the cyclohexane which vaporizes. Additionally, cyclohexane is removed by steam stripping due to the water vapor generated in the MHW process. In addition, findings demonstrate that a minimum mass ratio of water/cyclohexane of 1/2 is enough to reduce cyclohexane concentration to undetectable levels (150ppm) after 780 seconds, in agreement with the previous literature. Therefore, a water/cyclohexane mass ratio of 1/2 was employed to investigate the removal rate of cyclohexane for samples with fine concentrations of 10 and 20 wt% as well as cyclohexane concentrations of 6 and 12 wt%. The experimental data reveal an excellent agreement with a simple Lewis exponential drying model. Moreover, regardless of the initial cyclohexane concentration, a higher fine content results in a shorter vaporization time and a faster solvent removal rate. Fine particles exhibit a specific surface area significantly higher than coarse solids. Therefore, this behavior is attributed to an improvement in heat transfer efficiency promoted by an increased contact area between the heating agent or microwave absorber (water) and the sample. Such results demonstrate an improvement compared to conventional heating which is approximately 3 times slower for low-grade ore (higher fines content). The initial cyclohexane concentration, however, did not substantially affect the removal rate at the same fine concentrations. Overall, the findings show that MWH can effectively remove cyclohexane from NAE gangue, meeting economic and environmental constraints, laying the foundation for developing a greener NAE technology, and supporting the efforts of the oil sands industry to achieve net zero emissions.

Acknowledgements

I am grateful for the opportunity to work on this project. I am very fortunate to have the chance to work with my supervisors Dr. Phillip Choi, Dr. Stanislav Stayoanov, and Dr. Qi Liu. Thank you very much for the countless meetings to guide me through this study, all discussions, pieces of advice, and guidance.

I am thankful to the Institute for Oil Sands Innovation (IOSI) for providing access to the lab equipment. The experiments conducted in IOSI Labs were essential to obtain the results and insights found in this thesis. Special thanks to the IOSI team, Lisa Brandt, Brittany Mackinnon, Dr. Ni Yang, Dr. Natalia Semagina, and Dr. Xiaoli Tan for the access to the lab equipment, assistance on training, guidance on equipment setup, and insights throughout this project.

I would also like to thank Dr. Zaher Hashisho for providing access to the microwave setup and training.

I extend my acknowledgment to Future Energy Systems for the project funding.

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List of Abbreviations

$\approx$	Approximately
χ^2	Chi-square
^{2}	Coefficient of determination
ε''	Dielectric loss
ε'	Permittivity
ε^*	Complex permittivity
ε_0	Free space permittivity
ε_r	Relative permittivity
$Bit.C$	Bitumen Carbon
CH	Cyclohexane
$CHNS$	Carbon, Hydrogen, Nitrogen, and Sulphur elemental analysis
$CHWE$	Clark Hot Water Extraction
CR	Ratio of cyclohexane
D_p	Penetration depth
$DSBS$	Dry Soxhlet Bitumen Solids
F	Fine particles

GC	Gas-Chromatography
$HPLC$	High-Performance Liquid Chromatography
LOD	Limit of Detection
LOQ	Limit of Quantification
$mBar$	Millibar
MWH	Microwave Heating
NAE	Non-Aqueous Oil Sands Extraction Gangue
P_{avg}	Power average
ppm	Parts Per Million
$RMSE$	Root Mean Squared Error
T	Temperature
t	Time
$tan\delta$	Loss tangent
W	Water
$WSBS$	Wet-Soxhlet Bitumen Solids

1. Introduction

Alberta's oil sands are the main resource of oil in Canada, accounting for 96 % of the total oil reserves and more than 70 % of the total Canadian oil production [1]. Oil sands is the name given to the rock matrix formed essentially by bitumen, water and minerals particles such as sand and clay minerals [2]. Bitumen is a highly dense, viscous heavy crude oil primarily composed of high-molecular-weight hydrocarbons with a low hydrogen-to-carbon ratio and rich in high heavy metals [2, 3]. Although comparable to heavy oil, bitumen has a higher viscosity, above 10 $Pa.s$, and density, roughly 1000 kg per cubic meter [4]. Due to bitumen's high viscosity, the fluids are essentially immobile in the reservoir [5]. As a result, bitumen from oil sands can not be extracted from the reservoir just through a mechanical process such as pumping, which typically occurs in conventional oil extraction. Therefore, special processes have to be employed in the extraction [6].

Even though the process of extracting bitumen from oil sands is inherently more complex and more expensive than the light conventional oil extraction, the so-called unconventional resources are essential to meet expected world oil and energy needs for the next decades [6, 7]. The world population is expected to pass 9 billion people by 2040. This growth will profoundly impact the world's energy needs by increasing 40 % of energy demand in 20 years [8]. On the other hand, discoveries of new conventional oil reservoirs are not following this growth in demand [7]. Therefore, non-conventional oil extraction assumes an important role in the international energy panel. In this scenario, the study of new technologies to improve bitumen extraction becomes strategic, particularly, in countries like Canada, and Venezuela which lead the unconventional oil production globally [7].

The oil sands bitumen recovery process depends essentially on the depth of the reservoir. The so-called surface mining operations or open-pit mining are applied for deposits up to 75 meters under the overburden material, which is a layer of vegetation, clay, sand, and silt that covers the oil sands [2, 3]. The material is mined and transported to an extraction facility where the bitumen is separated from the sands. Differently, when the bitumen is too deep below the surface non-mining extractions known as *in-situ* processes such as Steam-Assisted Gravity Drainage (SAGD) and Cyclic Steam Stimulation (CSS) are employed [2, 3, 9].

In reality, the techniques are not interchangeable, and ideally, *in-situ* requires that the reservoir sits at least 200 m below the surface, while mining are typically in the range of 50-75 m below the surface [9]. Additionally, pilot systems that combine both methods are under study [3].

1.1 The Current Commercial Technologies

1.1.1 Open-Pit Mining

Surface mining is the oldest technique applied to recover bitumen from oil sands [2]. The process so-called the Clark Hot Water Extraction (CHWE) was first developed by Prof. Karl Adolf Clark (1888-1966), University of Alberta, in the mid-twentieth century. The process starts with the crushing of the mined ore, then it is mixed with hot water at an approximate temperature of 80 °C to obtain a 50 °C slurry mixture of water, sand, bitumen, and minerals. [2, 6, 10]. Next, the bitumen liberation takes place in a hydrotransportation process from the slurry box towards the Primary Separation Vessel (PSV) [2, 6, 10]. The bitumen is released in droplets which are collected at the top of the vessel through an aeration and flotation process [2, 6, 10]. The collected bitumen froth continues to treatment to remove fine particles and water [2, 6, 10]. The remain mineral mixture which decants in the bottom of the vessel is discarded into tailing ponds [6, 10].

The Clark process was vital to launch the bitumen extraction from oil sands in the 1960s and 1970s by the Suncor and Syncrude oil companies [2]. The process has been studied and improved ever since and significant improvements have been achieved in the process, particularly in terms of lowering the required temperature of the slurry [11], and reducing the make-up water needed in the process [2]. However, the process still exhibits important limitations that mostly affect its performance in environmental terms, as follows:

(a) **Thermal energy involved with the water heating process and make-up water**. According to the Alberta Energy Regulator[12], roughly one billion cubic meters of water was used in the process of production of 630 million barrels of bitumen in 2019. Even though great improvements have been applied to recycle the water used in the process, it still demands approximately 20 % of non-saline of make-up water. Further, the CHWE process still demands a lot of energy for heating approximately 2 cubic meters of water per barrel of bitumen – recycled and make-up water combined –, which represents a high thermal energy consumption and greenhouse gas generation [2]. In addition, this 20 % of clean water comes from the Athabasca River, which is another environmental concern [2, 6, 12].

b) **Tailing Ponds**. The sediment slurry in the Clark process forms a fluid phase system that is discharged to tailing ponds. Approximately 50 % of the tailings content is water, and most of it is clarified and recycled in the process [2]. In fact, 70-80 % of the water used in the extraction process is reclaimed water from the tailing ponds. Additionally, the sand settles quickly, however, the fine particles form a fluid phase system, known as fluid fine tailings (FFT), that otherwise treated remain suspended for several decades [6]. Currently, the size of the tailings ponds is greater than 130 km^2 and might reach 2 billion cubic meters by 2033 if no substantial progress in the tailings management is achieved. [2, 6, 13]

c) **Low bitumen recovery from oil-wetted and low-graded reservoirs**. Although the Clark process exhibits bitumen recovery rates from high-grade ore above 90 %, it shows low performance for low-grade ore and ores from oil-wetted reservoirs [2, 6]. This must be addressed, as the water-wetted high-grade ore will naturally decrease in the future [6].

1.1.2 Non-Mining Techniques

The Clark process is a well established, and a very efficiency process, however less than 20 % of the oil sands in Athabasca oil sands – the Canadian oil sands reserve– are placed near the surface enough to be mined [2, 3, 14]. In this context, non-mining *in-situ* techniques have been gaining ground, and since 2012 *in-situ* extraction processes have been producing more barrels per day of bitumen than mining activities [15].

1.2 Non-aqueous solvent extraction processes

Alternatively, to address the water-based processes environmental limitations and to enhance the low-grade bitumen recovery, non-aqueous bitumen extraction techniques or NAE might be the solution [6]. NAE processes replace water for other solvents, which might be a full or a partial replacement, aiming at reducing the make-up freshwater usage, the tailing ponds environmental concerns as well as creating opportunities for bitumen extraction from low-grade ores [6].

Currently, the new waterless-based technologies are still under investigation, but NAE is not a new process, it has been studied for decades. Even though the most advanced NAE processes are still in the pilot scales, the constant intensification in environmental regulations have been drawing attention to this alternative in the past years [6].

Technologies based on the Clark method are well established in the industry, they have excellent efficiency in recovering high-grade bitumen with constant improvement in reducing make-up fresh water [2]. In this sense, to be seen as a potential commercial substitute for the process in the industry the NAE process under study must be able to have a good performance in terms of: (a) low thermal energy required, which would reduce the emissions in the bitumen extraction activities – CHWE requires solvent (water) temperature above 50 °C –; (b) decreasing the water usage in the process; (c) addressing the tailing pond problem by eliminating it or at least reducing it drastically; (d) keeping the efficiency in recovery high-grade bitumen focusing on improvements for low-grade bitumen oil sand ore [6]. Lin *et al.*[6] reviewed the literature and observed four main processes for bitumen extraction (a) solvent-alone extraction or SAE, (b) Solvent extraction spherical agglomeration or SESA, (c) ionic liquid assisted solvent extraction or ILASE, and (d) switchable hydrophilicity solvent extraction or SHSE.

1.2.1 Solvent-alone extraction

The solvent alone process (SAE) is one of the main wateless process developed for oil sands bitumen extraction [6]. The primary process was proposed by Cities Service Athabasca Ltd almost 50 years ago [6, 16]. Decades later, several improvements and changes have been applied in the SAE original process, however, the fundamental process may be described as Figure 1.1 illustrates.

According to the flowsheet illustrated by Figure 1.1, first, the mined ore is fed into a digestion vessel at the same time as the organic solvent. Then, organic extraction of bitumen from the ore is taken place in this vessel. Next, the mixture of dissolute bitumen, and the solid phase is transferred to a multistage solid-liquid separation to separate the bitumen phase from the mineral solid phase. This separation occurs through a gravity sedimentation process. In each process step, the dissolute bitumen stream is collected in the top stream of each separation vessel and it is sent to the clarification process to remove fine particles present in the dissolute bitumen. The bottom stream of each process is continuously sent to the next phase to enhance the bitumen recovery [6, 16].

In the clarification process, the fine particles might be removed by a mechanical process such as centrifugation and filtration or through a polymer adsorption process [6]. This process is crucial in bitumen extraction, as there is a high strict pipeline transport constraint for the solid fraction in the commercial bitumen [2, 6]. The top flow from this stage undergoes a final solvent recovery process, at which a distillation process takes place to separate the bitumen from the solvent [6]. The bottom stream known as *wet-gangue* is sent to a solvent recovery phase, the method employed can be either a drying or a stripping process [6]. The final flow known as *gangue* is the tailing for this process, and the solvent recovered streams are recycled in the process [6]. Solvent losses in the gangue and lack of environmental impacts are challenges of these technologies as well to obtain a clean bitumen product with fine particles within the pipeline constraints [6, 17].

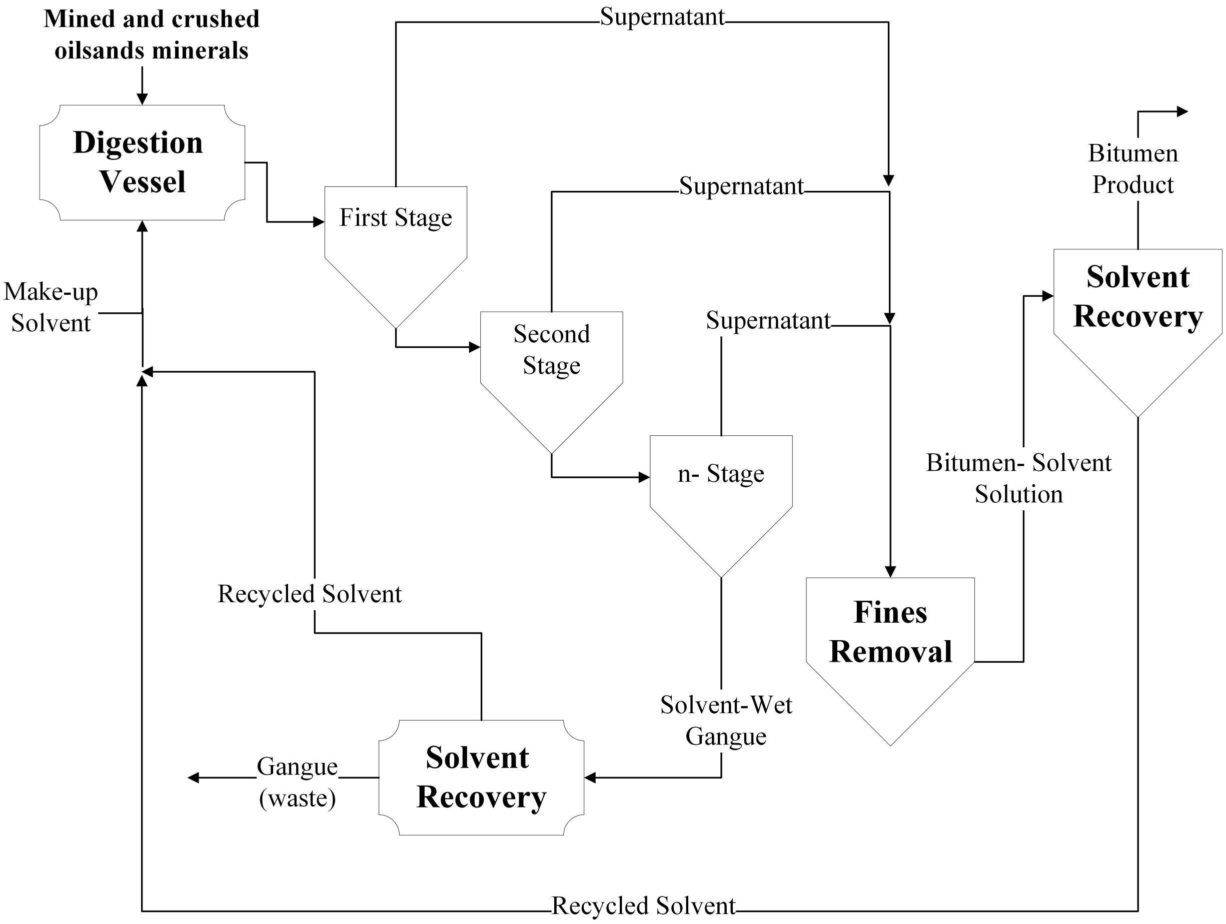


Figure 1.1: Solvent alone bitumen extraction process. Adapted from [6, 16]

1.2.2 Solvent extraction spherical agglomeration

Agglomeration is a process in which a solvent is added to a suspension to work as a binder between suspended particles and drive them to agglomerate by the action of agitation[18]. In other words, in agglomeration, a solvent is added to break a colloidal suspension helping in the clarification process. In this sense, this technique might help to address the greatest challenge in SAE: the process is the removal of fine particles [6, 18].

In the solvent extraction spherical agglomeration (SESA), first, the organic solvent is added and the extraction of bitumen from oil sands happens in the same way as the SAE process. Later, low quantities of water are added to the suspension formed by bitumen, organic solvent, and fine particles [6, 18]. As fine clay particles are hydrophilic, when water is added – under some agitation process [18] – it acts as a ”glue” to bring the particles together. In this manner, as the bitumen and the organic solvent are hydrophobic the SESA process promotes an efficient separation between the finely dispersed particles and the solvent-bitumen medium [6, 18].

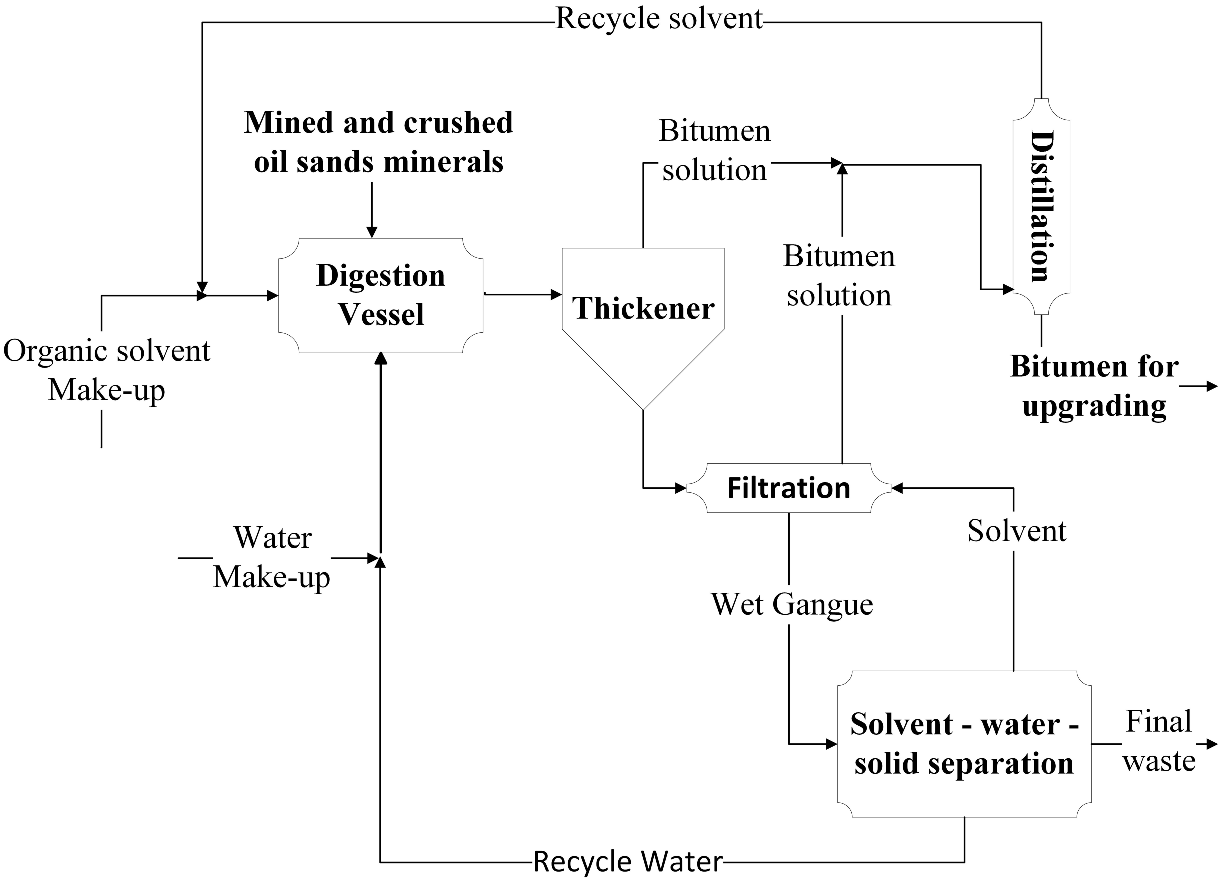


Figure 1.2: Solvent extraction spherical agglomeration. Adapted from [6, 16]

Even though the SESA processes reported in the literature show many differences from each other, there are typical steps present in SESA process as described by Lin *et al.*[6] As shown in the Figure 1.2, the mined ore, solvent, and water are added to the digestion vessel. Next, the mixture undergoes thickening where the diluted bitumen is recovered and then it is sent to distillation to recover the solvent. The underflow goes to a filtration process in which the organic phase is recovered and sent to the distillation process. The aqueous phase is sent to a stripping unit where the water is recovered and recycled from final gange.

1.2.3 Ionic liquid assisted solvent extraction

Currently, the ionic liquid assisted solvent extraction or ILASE process is still under development, bench and pilot scale works have been reported in the literature [6, 19, 20]. According to Painter *et al.*[19] and Li *et al.*[20] the ILASE process has great advantages. It addresses the greatest challenge of the SAE method as it delivers a bitumen with no fine particles detectable in infrared spectroscopy at the same time as it solves the problem of the tailing ponds as it generates a dry mineral waste. Also, the process occurs at room temperature and it does not use any water other than to extract recover the solvent. In addition, the ILASE process enhanced the extraction of larger fractions of bitumen in comparison to the solvent alone extraction process. Figure 1.3 illustrates the process. First, crushed and mined ore is added to the digestion vessel along with the ionic and the organic solvent. The ILASE extraction generates a three-phase system. The lightest phase, consisting of dissolved bitumen in the organic solvent, the medium phase is formed by the ionic solvent, and a mixture of ionic solvent and mineral solids at the bottom. Next, the organic phase is separated from the inorganic phase and the solids. The organic phase goes through solvent-bitumen separation, and the solids are washed with water which is easily separated from the IL and both can be recycled.

As discussed, the application of ionic solvents in the oil sands industry has great potential to address the current environmental challenges of the CHWE process. In addition, ionic solvents have great advantages, as they are not inflammable and volatile at room temperature [6, 19]. However, ionic solvents are very expensive materials [6, 19], and the study of the toxicity of ionic solvents is still in its incipient stages with no sufficient information about their potential harm [6].

1.2.4 Switchable hydrophilicity solvent extraction

The Switchable Hydrophilicity Solvent Extraction or SHSE process employs a solvent that can switch between a hydrophilic solvent form to a hydrophobic solvent form as reported by Holland *et al.*[21]. As discussed by Lin *et al.*[6], the process starts with the addition of the hydrophobic form of the switchable-hydrophilicity solvent (hydrophobic-SHS), which promotes

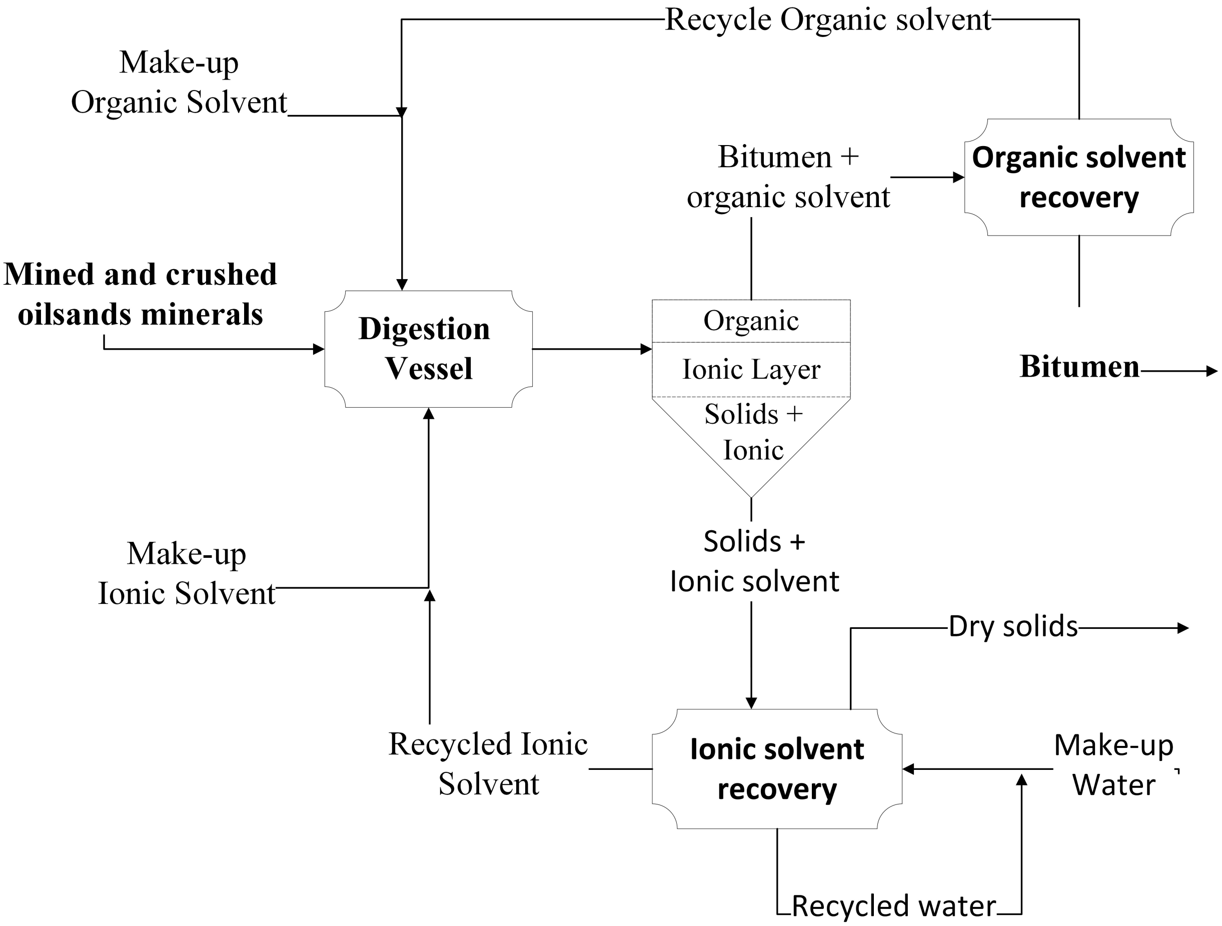


Figure 1.3: Ionic liquid assisted solvent extraction. Adapted from [6, 16]

the bitumen extraction from the mined ore. Next, the organic phase is separated from the wet-solid phase by physical means. The organic phase is mixed with CO_2-carbonated water, which changes the solvent to its hydrophilic form, promoting the ready separation between the hydrophilic-SHS and the bitumen. The hydrophilic-SHS goes back to its hydrophobic-SHS by expelling the CO_2, which easily recovers the water and the hydrophobic-SHS to recycle. The wet-solids are treated with a similar hydrophobic-hydrophilic changing process.

In that sense, the SHSE process does not require any distillation step which reduces the energy and greenhouse gases involved in the SAE process. Also, the SHSE process recovers both high and low-grade oil sands with efficiency above 95 % [21]. In addition, there is no fine particles in the bitumen obtained by this process, on the other hand, it is challenging to remove the residual solvent from the bitumen obtained in the process [6].

1.3 Main Challenges in NAE implementation

The success of the implementation of the NAE methods rely upon two major factors:

a) Addressing the environmental impact of the tailings generated by the current water-based technology by generating dry tailings [6]. Further, providing dry tailings free of solvent, both due to environmental concerns of releasing organic solvent in the environment and to economic reasons as the solvent is more valuable than the bitumen itself [22]. In this sense, the organic solvent must be recovered and recycled in the NAE process.

b) Delivering a diluted bitumen with a concentration of solids and connate water combined lower than 0.5 wt% to match the pipeline and refinery requirements [2, 6].

Nikakhtari *et al.*[17] investigated several light hydrocarbon solvents for NAE and concluded that cyclohexane combined a high bitumen recovery, low residual solids in the product bitumen, and low residual concentration of solvent in the gangue. Nonetheless, up to the date of this study, there was not any NAE commercial plant in operation, thus no regulations for solvent disposal were available. However, the current government regulations in Alberta for solvent residue in the tailings produced by the bitumen froth treatment in the Clark process is 4 parts of solvent for every 1000 parts of bitumen produced [6, 17, 22]. Additionally, according to Nikakhtari *et al.*[17] the current performance of the companies is 3 m^3 of solvent for each 1000 m^3 of bitumen. In this manner, the authors suggest that 260 parts of solvent to a million parts of tailings (water-free basis) would surpass the actual industry performance. Further, the current environmental and technical information for problem spills in place for cyclohexane in Canada indicates a odor threshold range from 25 to 370 ppm, and a Threshold Limit Value (TLV) for humans is 300 ppm [23]. Even though further studies regarding the safe use of cyclohexane in an industrial scale of NAE process are necessary [17], values like these might be used as a reference to drive the solvent recovery goals in the NAE processes under development [6, 22].

Previous works studied the recovery of cyclohexane from the gangue by employing air and vacuum drying techniques [24–27]. Ambient air drying is effective and inexpensive as it relies mainly on capillarity forces, however, it takes hours to achieve a few hundred ppm of residual cyclohexane in the gangue [27]. Increasing temperature and decreasing pressure can reduce the time needed to achieve residual cyclohexane to 250 ppm from hours to minutes [26]. For example, drying gangue from high-grade ore at 95 kpa and 90 °C can achieve 250 ppm after about 700 seconds [26]. However, under the same conditions, low-grade ore samples dry approximately 3x slower [26]. Additionally, as gangue samples are mainly formed by solids conventional heating of the gangue samples on a large scale would be excessively costly for an industrial NAE process [28], particularly in a vacuum environment.

Microwave Heating (MWH) has been identified as a possible solution due to its selective and rapid heating nature [28, 29]. Additionally, NAE gangue is a non-polar mixture of soil and organic solvent which makes it a poor microwave absorber [28, 29]. In this manner, water can simply be added to the sample to absorb microwaves and act as a heating agent, therefore transferring energy to cyclohexane quite more efficiently than the conventional heating techniques [28–30].

Along with the solvent recovery from the NAE gangue, achieving the standards of solid and water in diluted bitumen is crucial to create a process attractive to the market [6, 22]. The actual performance of fine removal in the most advanced NAE processes is not able to achieve these standards yet, the diluted bitumen from these processes has roughly 0.5-3 % of fine particles [6]. In this sense, fostering studies in solvent recovery and fine particle removal is strategic to lay the foundation for developing a greener NAE technology, and supporting the efforts of oil sands industry to achieve net zero emissions.

1.4 Objectives and Project Scope

This project aims at studying microwave assisted drying methods applied to recovering organic solvent (cyclohexane) from gangue obtained from the NAE process of mined oil sand ore. In this manner, this work's main goals are:

1. Determine the optimum cyclohexane-water mass ratio to obtain cyclohexane concentrations below 250 ppm by applying microwave heating (MWH) to NAE gangue samples with different concentrations of cyclohexane, water, and fine particles [17, 26]. Table 1.1 summarizes the investigated scenarios.

Table 1.1: Summary of scenarios assessed in this work.

Sample	**Cyclohexane (wt%)**[1]	**Water (wt%)**[2]	**Fines (wt%)**[3]	**Bitumen (wt%)**[3]
CH06_W02_10F	6	2	10	1
CH06_W03_10F	6	3		
CH12_W04_10F	12	4		
CH12_W06_10F	12	6		
CH06_W02_20F	6	2	20	1
CH06_W03_20F	6	3		
CH12_W04_20F	12	4		
CH12_W06_20F	12	6		

[1] wt% in wet basis.
[2] wt% in dry basis.
[3] wt% based on soxhlet solids only.

2. Determine the residual concentration of cyclohexane in each sample after undergoing microwave heating (MWH) using gas chromatography with an internal standard method, ensuring a lower limit of quantification limit of at least 250 ppm.

3. Obtain an experimental curve of the drying rate of cyclohexane at the optimal cyclohexane-water mass ratio for samples with low and high fines content, and low and high concentrations of cyclohexane.

4. Determine a model that can describe the rate of drying behaviour of MWH applied to NAE gangue.

Further discussion about improvements on the quality of the diluted bitumen product is beyond the scope of this work.

2. Literature Review

2.1 Current Advances In Organic Solvent Recovery From NAE Gangue

Nikakhtari *et al.*[24] investigated the removal of cyclohexane from non-aqueous extracted gangue samples obtained from high-grade oil sands ore. Samples were dried by applying air drying in a fumehood or within a controlled environment chamber. The work quantifies the residual cyclohexane and removal rate for samples dried at different temperatures and relative humidities. In addition, the authors studied the influence of adding water during the NAE on the gangue drying process. They found that the samples dry in two stages, the first is governed by a rapid evaporation of cyclohexane and the second by a slow evaporation of mostly water. Additionally, the findings show that the rate of removal of the solvent increases with temperature but decreases with relative humidity. Further, they observed that high concentrations of water in the NAE gangue increase the residual cyclohexane.

Panda *et al.*[27] studied the effect of residual bitumen on the cyclohexane removal from NAE reconstituted gangue samples obtained from rich-grade oil sands ore. Samples were dried on a scale in a fume hood for 2 hours and the residual cyclohexane was obtained by a quartz inert capillary mass spectrometer (QICMS). They concluded that the rise of bitumen-cyclohexane solution through the gangue sample is mainly due to capillary. Additionally, samples with higher residual bitumen concentration showed decreased capillarity which led to a slower rate of solvent removal.

Renaud *et al.*[26] performed experiments on vacuum drying of NAE gangue from low and high-grade oil sand ore. Drying temperatures ranging from 25 to 105 °C and pressures from 30 to 95 kPa were examined. A Dynamic Sampling Mass Spectrometer (DSMS) was utilized to obtain the concentration of cyclohexane and water during the drying experiments. They observed that either an increase in temperature or a decrease in pressure improves the cyclohexane evaporation. Nonetheless, the results show that at the same pressure and temperature gangue samples from low-grade ore required a time approximately three times longer than the time observed in high-grade ore to achieve the same target of 250 ppm of residual cyclohexane. The authors suggest that the larger portion of water and fine particles present in the low-grade ore probably obstruct the pores blocking cyclohexane evaporation.

Khalkhali and Choi[25] studied the effect of varying the concentration of residue bitumen, fine particles, and water on ambient air drying of reconstituted gangue with 12 wt% of cyclohexane. The drying experiments were carried out inside a fume hood for 2 hours. They observed that water plays an important role in the air-drying process, where high contents of water yielded a porous obstruction blocking cyclohexane evaporation. Likewise, the authors concluded that samples with no water also showed insufficient cyclohexane evaporation due to poor cyclohexane film formation. One of the reasons why the presence of water facilitates cyclohexane film formation is that the presence of water reduces the available surface area for cyclohexane wetting [31]. Consequently, this results in the formation of thicker and more stable cyclohexane films [31]. Regarding the effect of fines, Khalkhali and Choi[25] did not observe a significant impact on the air drying process by doubling the fines content. Results for porosity measurements revealed lower porosity for high fines samples compared to low fine samples, which should lead to a decrease in the initial cyclohexane drying flux. Nevertheless, as the hydrophobicity increased in samples with higher fines content, the cyclohexane film formation was favored. Therefore, the authors concluded that one effect neutralizes the other, thus the cyclohexane air drying rate showed no significant effects due to varying the fines content.

In general, most of the previous studies investigated solvent recovery by applying air drying techniques [25, 27, 31, 32]. Results indicate that the concentration of cyclohexane in the NAE gangue from concentrations around 12 wt% to the order of tens or hundreds of ppm in a matter of hours. Additionally, the time to reach low concentrations of cyclohexane in the gangue can be substantially reduced under certain vacuum and/or conventional heating conditions [26]. Nevertheless, applying any sort of conventional heat throws away large amount of energy as the solids which account for 80 - 90 wt% of the total gangue mass also heated [28].

In this sense, Khalkhali *et al.*[28] investigated that cyclohexane can be effectively recovered from the NAE gangue by applying microwave heating (MWH). Results demonstrate that both cyclohexane and DSBS solids are poor microwave absorbers, however, water can be effectively used as a microwave absorber and therefore as a heating agent for the samples. In this manner, the authors investigated the effect of microwave heating on reconstituted gangue samples with a constant content of fine particles, residual bitumen, and cyclohexane varying the amount of water (4, 6, and 12 wt%). Results indicate that the concentration of cyclohexane in samples containing a water/cyclohexane ratio of 1/2 was reduced to undetectable levels after 780 seconds of microwave heating. Thus, the findings reveal a great potential for applying MWH to remediate NAE gangue tailings in a rapid and selective, and therefore, energy and economic efficiency manner. Nonetheless, the MWH applied to NAE gangue is still in the early stages of development, requiring a broader understanding of the performance of MWH when varying the solvent, fines, and bitumen content in the samples.

2.2 Microwave Heating

2.2.1 Advances in Microwave Heating

Heating processes are more than common in the industry, particularly, in the chemical industry. Whether a physical change or a chemical transformation of a substance takes place in a unit of process or operation, heating is more than likely necessary to perform the procedure. However, conventional heating-based processes are extremely energy-consuming. Data from US Energy Information Administration, Annual Energy Outlook 2018 show that bulk chemicals and refining activities together – where heating units are widely present in the processes – account for 50 % of the energy consumption of the whole industrial sector [33]. Among these processes, distillation, the main separation method applied in the chemical industry, is responsible for 40 % of the total amount of energy spent in the chemical industry [33].

In fact, the presence of these high energy-consuming processes in the chemical industry maintains constant and wide efforts to enhance the energy efficiency in the plants to decrease the energy intensity of these processes [33]. In reality, great results have been achieved, in the period between 1990 to 2015 the amount of energy spent per unit of production decreased by almost 60 % in the European chemical industry [33]. On the other hand, the demand for chemicals increased by 85% [33], which highly increased the total amount of energy needed in the processes, even though the amount of energy per unit of product delivered has been declining. In this sense, studies to improve the energy intensity in the chemical industry are essential, both to keep the industry financially competitive and to foster the chemical manufacturers to address the environmental regulations [34]. In this context, since microwaves have the ability to selectively heat matter, microwave-assisted methods might be employed to enhance energy efficiency in chemical industry processes [34].

The first application of microwaves was reported in the military industry back in World War II during the development of radar systems, and ever since the list of applications of this electromagnetic radiation did not stop to grow [35, 36]. Heating, satellite communication, Bluetooth technology, radar, power transmission, navigation, cancer treatment, weather control, etc. are examples of current applications of microwaves [35]. In general, due to the ability to "concentrate the heat", the main application of microwaves in the chemical industry is in processes that require any form of heating.

In the context of chemical reactions, microwaves have been widely reported in the literature in organic synthesis such as condensation, oxidation, polymerization, cross-coupling, alkylation, heterocyclization and many others [37]. Nevertheless, microwaves do not carry enough energy to induce a reaction as it happens in photochemical reactions due to energy absorption of visible and ultraviolet light [38]. The energy of microwaves must first be converted into heat by a microwave absorber in the medium [38]. Microwaves can be tuned to drive the energy directly to a particular type of molecule [39]. As a result, the reaction time is reduced, and as a consequence, the side reactions are minimized and significant improvements in selectivity and reaction yield are observed in microwave-catalytic processes.[39]. Further, microwaves have shown promising results in carbothermic reduction reactions of metal oxide to metals, improving the process efficiency in contrast with the traditional heating technology applied in the mining industry [40]. Moreover, microwaves can perform great improvements in processes and operations that involve traditional heating such as drying, anhydration, thermal waste remediation, materials fracturing and etc. [35, 40–42].

Microwave heating transfers the heat through the material electromagnetically instead flowing as a conventional heat flux [43]. Thus, the heating rate of material exposed to microwaves is not limited by thermal diffusivity [43]. Therefore, the heat distribution is highly improved by reducing the typical heating time to less than 1 % of typical conventional heating [43, 44]. Therefore, microwave heating has been studied as an efficient option for contaminated soil remediation as an option to conventional thermal treatment [29, 43, 44]. Studies have shown that soils can be poor MWH absorbers which allows the microwaves to penetrate into the samples [29]. Nevertheless, small concentrations of MWH absorbers within the soil sample such as water can act as a heating agent promoting a large increase in the sample heating and therefore the contaminant removal [29].

Chen *et al.*[45] studied the microwave-assisted remediation of soil contaminated with light and heavy crude oil. In the work, 10 g ca. of silty loam contaminated soil (particle size $10-50$ μm) underwent MWH for $5-20$ minutes with powers ranging from 200 to 1000 W. Results indicated that light and heavy oil can be removed from the soil samples after 15 and 20 minutes of microwave heating at 1000 W with a removal efficiency of $\sim$ 99 and 96 %, respectively. Moreover, the final concentration of the contaminants in the samples contaminated with the light oil dropped from approximately 13,000 to 140 ppm, and the heavy oil from roughly 11,000 to 400 ppm. The authors also found a considerable reduction in the temperature needed to treat the soils with MWH compared with conventional thermal heating. The maximum temperatures observed during the MWH of the samples contaminated with light oil ranging from $\sim$ 350-400 °C and heavy from $\sim$ $350-400$ °C while the conventional thermal remediation requires $470-500$ °C. Moreover, they found that the MWH did not cause a substantial impact on soil organic matter (SOM) maintaining the soil fertility at reasonable levels.

Falciglia *et al.*[46] studied the use of MWH to treat soils contaminated with PAHs (polycyclic aromatic hydrocarbon) which show a boiling point ranging from 200 to 600 °C. In the work, 20 g of contaminated soil is irradiated for $5-60$ minutes with power ranging from 250 to 1000 W. Overall, results showed a removal efficiency between 70 − 100 % for PAH and 10 minutes at 1000 W as the most efficient conditions, and 90 % achieved after 60 minutes at 440 W for N-PAH removal. Results indicated that contaminant properties, such as soil adsorption affinity and polarity affected the removal efficiency. The authors also discuss that due to the high dielectric loss factor of PAHs the microwave energy can be selectively absorbed by these contaminants which promote a selective temperature increase of the adsorbed PAHs. Consequently, substantial contaminant removal happens at an overall soil temperature significantly below the boiling point of the investigated PAHs. Therefore, they observed the removal of contaminants with boiling points ranging from 255 − 448 °C regardless of the bulk soil temperatures were recorded between 115 − 205 °C, which suggests selective heating as one of the possible mechanisms of removal of PAHs from contaminated soils. Moreover, samples with a moisture of 10 % showed better removal efficiencies than dry ones, which indicates that contaminant stripping as a result of water vapour stripping as one of the PAH removal mechanisms. The authors also suggest thermal desorption vaporization, and molecular bond breaking as possible mechanisms.

Robinson *et al.*[47] investigated the use of MWH to extract bitumen from oil sands ore as an alternative route to current water-based technologies. In the work, samples of low and high-grade ore were MW irradiated. Findings suggest that the higher presence of water and fines in the low-grade ore allowed bitumen recoveries above 50 %. The authors discuss that hydrophilic fine particles are accountable for the higher water content in low-grade ore, therefore, both free water, which stands on the surface and within the grains, and bond water occurs in these solids. They suggest that the free water selectively heats by the microwave and vaporizes, however, the bond water maintains absorbing microwaves promoting a higher temperature (above 250 °C) and enhancing the bitumen recovery. Nonetheless, they suggest that small concentration of water in the high-grade ore (< 0.5 %) is only of a free water nature which was not enough to promote the heating sufficiently to recover bitumen at substantial levels. Therefore, the results indicated that low-grade ore (higher fines and water content) exhibits a better interaction with microwaves than high-grade ore. Additionally, these results are significantly industrially relevant as the current water-based technology does not have a good performance to recover bitumen from low-grade oil sand ore.

2.2.2 Fundamentals of Microwaves for Heating Processes

A charge in space generates an electric field, while a moving charge produces a magnetic field, these two fields combined form the broadly called electromagnetic field. An electromagnetic wave comprises of a combination of a magnetic and an electric field as a result of oscillating or moving charges. These two fields are perpendicular to the direction of the wave propagation, which travels into the air or vacuum at the same speed of light [36, 48]. Microwaves (MW) are electromagnetic radiation whose frequencies range from 300 MHz to 300 GHz, which lies in between radio and infrared frequencies in the electromagnetic spectrum [35, 36, 39, 41]. As an electromagnetic wave, microwaves can cause interference with other services, therefore to minimize this side effect the main common frequencies for microwaves in the industry are either around 900 MHz or 2450 MHz [43].

The interaction between a material and an electric field classifies the materials into two groups, the conductors and the insulators. Essentially, an insulator is a non-metallic material or in other words, a material that does not carry free moving charges. However, some insulators possess very few charges that can be polarized when exposed to an electrical field, this kind of material is well known as a dielectric [35, 36, 41, 42].

Conducting and insulant materials can either absorb or reflect the electrical component of microwaves [35]. In this sense, materials can be categorized into the following groups:

(a) **Opaque or reflective:** Opaque materials are those that reflect microwaves, or in other words, when irradiated by microwaves reflective materials do not allow microwaves to pass through. In general, this property is observed in conductors like metals [35, 49, 50]. In a sense, this reflective property of metals is a useful application in microwave-processing as microwave shielding [51].

(b) **Transparent:** Transparent materials show a minor interaction with microwaves. In reality, the reflection and absorption of microwaves in this kind of material can be neglected. This property is observed in non-conducting materials such as air, ceramic, glass, etc. [35, 49, 51]

(c) **Absorbing:** Absorbing materials show the capability of interacting with the electrical field of microwaves and absorbing the wave energy converting it into heat. These materials are also known as lossy dielectric materials [35, 49].

(d) **Magnetic:** Materials that can be heated by interaction with the magnetic component of the microwaves are denominated magnetic materials [35]. Further discussions about magnetic materials are beyond the scope of this project.

In microwave heating of dielectric materials, the energy transferred from microwaves to the material is essentially a result of the interaction between the dipoles of the material and the electrical field present in microwaves [35, 41, 42]. In this manner, the effects of the magnetic field in the process of microwave dielectric heating can be disregarded [35].

Out of the range of an electrical field, the dipole moment in a dielectric material is randomly orientated [52]. However, in the presence of an electrical field, the electrostatic coupling between the electric field and the dipole moments create a torque in the dipoles which attempt to align themselves with the electrical field direction, and consequently, polarizing the material [52]. A microwave electrical field alternates in a frequency in the order of MHz or GHz, therefore the direction of the microwave electric field changes at least millions of times per second. As a result, the dipole momenta in a dielectric material exposed to a microwave are constantly attempting to align themselves with the alternating direction of the electric field [43, 52]. Therefore, the constant friction within the material dissipates energy in a form of heat [43, 52], the process is called microwave heating (MWH) or dielectric heating.

An electromagnetic field is the result of an electric field created by a stationary charge and a magnetic field generated by a moving charge or an electric current. The interaction between these two fields is described by the well-known Maxwell's equations. The general theory for these equations can be obtained from electromagnetic textbooks and a better understanding of this theory applied to dielectrics is available at Hippel and Morgan[53].

This text, however, aims to discuss the key points of the electromagnetic theory to support the observations in microwave heating process. From this perspective, the main electromagnetic properties of the dielectric materials that govern the microwave-assisted heating process mainly discussed in the Literature are **relative permittivity, power dissipated, and penetration depth** [35, 41, 50].

2.2.2.1 Permittivity

Dielectric is a material that is capable to store energy under exposure to an external electrical field [52]. Figure 2.1 represents a parallel plate capacitor filled with a dielectric material exposed to an electrical field produced by a direct current (DC).

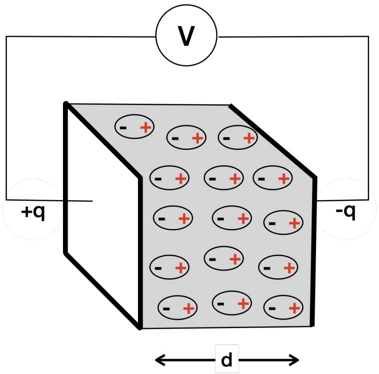


Figure 2.1: A parallel plate capacitor Adapted from [52].

The capacitance of the capacitor is given by Equation 2.1, A represents the area, d the distance between the plates, and ε the permittivity of the material between the plates.

$$C = \varepsilon \frac{A}{d} \tag{2.1}$$

Throughout time, the electrical field will align the dipole in the material. Therefore, the permittivity or dielectric constant is defined as the physical property that quantifies the capability of a material to polarize when subjected to an external electrical field [35, 41, 42, 52]. The absolute permittivity of a material ε' is given by the product of the free space permittivity ε_0 and the material's relative permittivity ε'_r as expressed by Equation 2.2

$$\begin{gathered} \varepsilon' = \varepsilon_0 \varepsilon'_r \\ \varepsilon_0 = 8.854 \times 10^{-12} \tfrac{F}{m} \end{gathered} \tag{2.2}$$

When a dielectric material is exposed to an alternating sinusoidal current (AC) part of energy from the current will charge the dielectric capacitor and part dissipate.

While electromagnetic waves are commonly represented by trigonometric functions, complex numbers are a convenient method to express these phenomena mathematically [52]. In this manner, the permittivity of a dielectric material exposed to an electromagnetic field is represented as a complex number, the complex permittivity ε^* [35, 52]. Therefore,

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \tag{2.3}$$

In Equation 2.3, the material dielectric constant ε' represents the degree of polarization observed in the material under the influence of an external electrical field [52]. This term can be interpreted as the stored electromagnetic energy in the material [54]. The term ε'' is known as dielectric loss, which accounts for the electrical energy converted to heat [52].

As a complex number ε^* can be expressed in terms of the magnitude of ε' and ε'' and the phase angle between them [35, 43, 52]. Figure 2.2 shows the complex permittivity represented in imaginary and real axis. There is a phase angle δ between ε' and ε'' which accounts for the difference between the capability of being polarized and losses observed as a result of being exposed to an oscillating electrical field [35, 52]. Thus, the ratio of ε'' and ε' also known as loss tangent (Equation 2.4) demonstrates the efficiency of a dielectric material to convert absorbed electrical energy into heat [35, 52]. In other works, the loss tangent is the ratio between the energy lost by the energy stored per cycle [52].

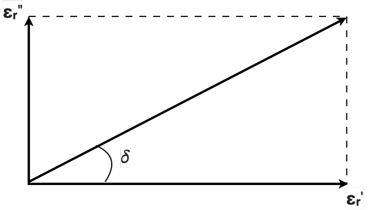


Figure 2.2: Complex diagram to represent the loss tangent. Adapted from [52].

$$tan\delta = \frac{\varepsilon''}{\varepsilon'} \tag{2.4}$$

Dielectric properties are a function of temperature and frequency and also vary with composition, moisture content, and presence of impurities [43, 52, 55].

2.2.2.2 Power Dissipated

Electromagnetic energy is absorbed into the dielectric and converted into heat as the electromagnetic wave spreads through the material in a process called power dissipation [35, 43, 55].

Equation 2.5 shows the average power dissipated due to the electrical losses per unit of volume, as derived by Metaxas and Meredith[55]. If the material in the study demonstrates significant magnetic properties, a magnetic loss term should be included in Equation 2.5 [55]. For simplicity, this term was not added to Equation 2.5 as this work aims to study the effect of microwaves on dielectric materials.

$$P_{avg} = \omega \varepsilon_0 \varepsilon''_{eff} E^2_{RMS} \tag{2.5}$$

Substituting $\varepsilon_0 = 8.854 \times 10^-12 F/m$ and $\omega = 2\pi$ yields:

$$P_{avg} = 0.556 \times 10^{-10} f \varepsilon''_{eff} E^2_{RMS} \tag{2.6}$$

Where P_{avg} is the average volumetric power dissipated. As observed in Equation 2.5, the power dissipation average is given in terms of the root mean square of the electric field E_{RMS} and effective relative dielectric loss factor ε''_{eff}. Where ε''_{eff} combines the losses due to conduction and polarization [35, 55].

2.2.2.3 Penetration Depth

Power is dissipated when the electromagnetic wave penetrates the dielectric material, the depth at which the power falls to $(1/e)$ (36.8 %) of the value observed at its surface is defined as penetration depth [35, 43, 52, 53, 55]. Equation 2.7 presents the penetration depth as derived by Metaxas and Meredith[55]:

$$D_p = \frac{\lambda}{2\pi\sqrt{2\varepsilon'}} \frac{1}{\left[\left(\sqrt{1 + \left(\frac{\varepsilon''_{eff}}{\varepsilon'}\right)^2} - 1\right)\right]^{\frac{1}{2}}} \tag{2.7}$$

where λ is the electromagnetic wavelength. For low-loss dielectrics, which $\frac{\varepsilon''_{eff}}{\varepsilon'} \ll 1$ Equation 2.7 can be approximated to Equation 2.8 [43, 55]. The error observed in the approximation is lower than 10 % [43].

$$D_p = \frac{\lambda\sqrt{\varepsilon'}}{2\pi\varepsilon''_{eff}} \tag{2.8}$$

As observed in Equation 2.8, penetration depth is a function of frequency and dielectric properties. As frequency $\propto 1/\ \lambda$, as the frequency rises the penetration depth decreases. For distillate water at room temperature, the penetration depth drops from approximately 120 mm at 915 MHz to near 18 mm at 2.45 GHz [52, 55]. In terms of temperature, the penetration depth of distilled water increases with the temperature [52, 55], it is observed to rise from 1.8 cm at 25°C to 3.1 cm at 50°C and 5.4 cm at 90°C [52] at 2.45 GHz. However, in the presence of ions, the penetration depth is observed to decrease [52, 55], in a concentration of 0.25M of NaCl at 25°C and 2.45 GHz the penetration depth for pure water decreases to approximately 0.5 cm [56].

Horikoshi *et al.*[52] estimated the penetration depth for several solvents using Equation 2.7. At 2.45 GHz most of the solvents show shallows penetrations, within 10 cm for polar solvents. They observed that hot spots might arise in the reactors while conduction reactions due to the penetration depth of the medium inside the reactor. In this sense, the size of the reactor and stirring techniques might effectively reduce the temperature gradient in the medium of reaction, and one should consider these factors during the reactor design [52].

Regarding the oil sand ore sample, Robinson *et al.*[47] measured the complex permittivity (ε' and ε'') at 2.45 GHz for low grade oil sand ore (7.1 wt% bitumen and 4.3 wt% moisture) and high grade ore (20.4 wt% bitumen and 0.5 wt% moisture). For high grade ore, at room temperature, they observed extremely low values for both dielectric loss and dielectric constant, $\varepsilon'' \approx 0.02$ and $\varepsilon' \approx 2.4$, respectively. For low grade ore, the measured values were $\varepsilon'' \approx 0.22$ and $\varepsilon' \approx 2.6$. Based on these values and Equation 2.8, the penetration depth for the oil sand ore can be as high as 150 cm for the highest grade and as low as 15 cm for the lowest. As observed by Nikakhtari *et al.*[57], the water content is inversely proportional to the ore grade, in that matter the more moisture in the oil sand sample the shallower the penetration depth is expected to be.

The microwaves are expected to cross the reactor used in this work with no further problems as it has a diameter of just 19 mm. However, the penetration depth of gangue should be a concern during the future scale-up of the process [52]. As the penetration depth is a function of the frequency, lower frequencies might be advantageous to extend the ability of the microwaves to penetrate deeper in the gangue sands [58].

2.2.2.4 Heating Rate

The heating rate of a dielectric material exposed to an external electric field can be modeled as shown in Equation 2.9, as proposed by Metaxas and Meredith[55].

$$P = \frac{Q_h}{t} \tag{2.9}$$

Where the absorbed heat Q_h may be given by

$$Q_h = \frac{M_a C_p (T - T_0)}{t} \tag{2.10}$$

Substituting Equations 2.6 and 2.10 into Equation 2.9, the heating rate $\frac{T-T_0}{t}$ becomes:

$$\frac{(T - T_0)}{t} = \frac{0.556 \times 10^{-10} f \varepsilon''_{eff} E^2_{RMS}}{\rho C_p} \tag{2.11}$$

Where f is microwave frequency, ρ and C_p are the density (Kg/m^3), and the specific heat $(J/Kg\,°C)$ of the material, respectively. Therefore, the heating rate of a material is a function of the frequency of applied radiation, and temperature due to dependence of ε''_{eff} of temperature.

2.2.2.5 Effects of Frequency, Temperature, and Moisture in Microwave Heating

Frequency

Frequency has an important effect on the dielectric properties of materials, it has an important effect on both dielectric constant and dielectric loss factor [52, 54, 59]. Hence, according to Equations 2.4, 2.5 and 2.7 the dissipation factor, the power dissipated and the penetration depth are dependent on frequency. Horikoshi *et al.*[52] present data for dielectric constant ε', dielectric loss ε'', and $tan\delta$ for several solvents measured at 915 MHz, 2.45 GHz, and 5.8 GHz. They observed that the dielectric constant ε' decreases as the frequency increases. The dielectric loss factor ε'', is larger for higher frequency for most of the 23 solvents tested, water, cyclohexane, and toluene included. However, it is important to note that even though higher frequencies tend to grow the dielectric loss factor ε'', its absolute values for nonpolar solvents are still very low. While water shows a dielectric loss ε'' of 10 and 20 the values for cyclohexane are almost 0 and approximately 1 for 2.5 GHz and 5.8 GHz, respectively. Therefore, as the dielectric loss measures the capacity to convert microwave energy into heat in the material, polar solvents like water are still more efficient than nonpolar ones even in higher frequencies. Likewise, the power loss Equation (2.5) is directly proportional to the dielectric loss factor.

The complex permittivity can be described by Debye's model [52, 54, 55]. In this model, the dielectric loss ε'' and the dielectric constant ε' are written as a function of frequency, refractive index, and a term known as relaxation time that represents the typical time involved in the reorientation of the dipole moments to the external electrical field direction. [54]. Hence, a diagram of dielectric constant ε' and dielectric loss ε'' as a function of frequency can be obtained. In the diagram for water at 25 °C, the dielectric constant ε' tends to 78.2 at lower frequencies and approximately 5 at higher frequencies. The dielectric loss ε'', however, shows a maximum at 18-20 GHz and then tends to zero at both very low and high frequencies [54].

Regarding the dissipation factor $tan\delta$, according to the data [52], it increases with the frequency for most solvents such as water, cyclohexane, and toluene. In this manner, the efficiency of converting absorbed microwave energy into heat for these solvents is more satisfactory in higher frequencies.

As observed in Equation 2.7, the penetration depth is inversely proportional to the frequency of the incident microwave. For example, the penetration depth for water decreases from approximately 14 cm at 915 MHz, to nearly 2 cm at 2.45 GHz and less than 1 cm at 5.8 GHz [52]. At ambient conditions, cyclohexane, toluene and other nonpolar solvents show deep penetration (greater than 28 cm) in low frequencies such as 915 MHz and 2.45 MHz, but only and few centimetres (approximately 3 cm) in high frequencies such as 5.8 GHz [52].

An additional concern about frequency is that due to the difference in the dielectric properties, materials interact differently with microwaves. In fact, this gives microwave heating processes the ability to be selective and therefore more efficient than conventional heating [29]. In this manner, one should choose a frequency of work that does not cause unnecessary absorption of microwaves by needless compounds that would waste energy. For example, for drying a gangue sample one should set a frequency that does not promote microwave absorption by the solid matrix.

Temperature

Temperature is an important variable in microwave heating as the dielectric properties are a function of temperature. Robinson *et al.*[47] assessed the complex permittivity for different temperatures. They observed that for the low grade sample, in a range of 20-100 °C, the dielectric loss increases up to peak $T \approx 70\,^{\circ}\mathrm{C}$ where $\varepsilon' \approx 0.30$ then it drops rapidly to $\varepsilon' \approx 0.05$ when $T \approx 100\,^{\circ}\mathrm{C}$. The dielectric loss stays constant up $T \approx 100\,^{\circ}\mathrm{C}$ when it starts to rise again. For the high grade ore, no change in the dielectric loss is observed up to $T \approx 500\,^{\circ}\mathrm{C}$, when it starts to rise. The dielectric constant for both high and low grade slightly decreases from 20-100 °C, they do not vary much between 100-500 °C then it rises above 500 °C.

In this manner, both power loss and heating rate for oil sand ore with higher moisture content are favoured in with the increase of temperature up to around the boiling point of cyclohexane ($BP_{cyclohexane} = 80.7$ °C as observed in Equations 2.6 and 2.9. The oil sand ore free of water seems to be transparent to microwaves given the extremely low dielectric loss factor. Nevertheless, the penetration depth must decrease as the dielectric constant decreases while the dielectric loss increases, as shown in Equation 2.8. Therefore, during the planning of a microwave heating setup, one should observe how the dielectric properties vary in the range of the set of temperatures and how it will effect the interaction between the microwaves and the sample.

Moisture

Moisture content deeply impacts the dielectric properties of soils. The dielectric constant and the dielectric loss of soils observed in several studies increase with the growth in the water content. [60–62]. In this sense, water can be considered a successful susceptor for microwave energy in the processes of microwave heating [28, 29]

2.2.3 Advantages Of Microwaves Against Conventional Heating

As discussed in Section 2.1 air drying of NAE gangue might not be an efficient solution in a large scale industrial process. Therefore, heating the gangue might become a solution to adapt the process for industrial needs. Nonetheless, bitumen is a low-priced commodity, and adding conventional heating would cause the non-aqueous extraction to be economically unfeasible. In this manner, to support the hypothesis that microwave heating is a better solution for heating the gangue this Section discusses the advantages of MWH against conventional heating.

In conventional drying processes, the energy flows from the exterior layers of the material to the inner layers through heat conduction [43, 52, 63]. In microwave heating, however, the energy is directly transferred from the microwave source to the material [43, 52, 63]. In this manner, the energy transfer from the microwave source to the heating material is more efficient than conventional heating as the former does not rely on conventional heat transfer mechanisms as the latter [52, 63].

Further, unlike conventional heaters that lose part of the energy to the environment heating the whole walls of the reactor, for example, microwaves can selectively heat the target material [52]. As discussed in Section 2.2.2.5, different materials respond differently to microwave heating. Therefore, microwaves can be tuned to target a specific compound in a sample [52]. In microwave drying of gangue, the microwaves will heat the water which will transfer the energy to the residual cyclohexane, but not the whole solid soxhlet solids need to be heated as a conventional drying process would require. In this manner, microwaves can be considered an efficient electricity-powered technology to heat and dry solids. Therefore, the use of microwaves might help the bitumen-extraction industry to reduce greenhouse emissions and achieve the target net-zero emissions.

In a microwave drying process, the vapour pressure of the moisture in the solids rapidly increases within the pores of the solid which promptly leads the moisture from the inner layers to the outer layers of the wet solid [43]. On the other hand, Meredith[43] warns that excessive energy dissipation of MWH of dielectrics of high density, non-porous and brittle may induce internal boiling of the moisture causing extreme internal pressure that burst the material. At the first sight, craking the gangue should not be a problem, however, this warning should be considered during the scale-up studies of the process as vapor expansions might cause undesirable stress in the reactor structure or even it might evolve to an operational hazard.

Nonetheless, there are some challenges in microwave heating design that might not be a problem for conventional heating, such as penetration depth, and nonuniform heating [52]. Thus, due to the limitations of the penetration depth as discussed in Section 2.2.2.3, MWH might not apply to a system in a different scale, for example. Moreover, impurities can cause a rapid temperature increase either in samples or the reactors which might lead to the burning of the former or the fracture of the latter [52]. Therefore, selecting the proper material to build the reactor is critical [52], and monitoring the sample composition to avoid unexpected burns might be necessary.

3. Methodology

3.1 Reconstituted Gangue

The composition of the oilsands ore found in Athabasca is quite variable, the fractions of sand vary from 55 to 80 wt%, fine particles 5 to 34 wt%, bitumen 4 to 18 wt% and water 2 to 15 wt% [64]. In this manner, the performance of the non-aqueous extraction varies as a function of the ore sample, and different bitumen recoveries are observed [27]. Likewise, wide variability is observed in the composition of the gangue sample obtained from the NAE process [65].

Panda *et al.*[27] studied the influence of residual bitumen in the solvent recovery of organic gangue samples. In their work, the authors proposed a protocol to bypass this variable composition concern of the oilsand samples by generating a gangue with controlled fractions of water, bitumen, and cyclohexane. They named the controlled composition sample as **reconstituted gangue**.

In this context, aiming at studying the influence of water-cyclohexane ratio and fine contents in the microwave-assisted recovery of solvent from cyclohexane-wet-gangue, this work follows the preparation of reconstitute gangue procedure proposed by Panda *et al.*[27] to control the bitumen, water, and cyclohexane composition in the samples.

3.1.1 Materials

In this study, rich-grade oil sands ore was utilized to obtain the soxhlet solids to prepare the reconstituted gangue. The sample was courtesy of Syncrude Canada Limited. ACS grade toluene was used in the Dean-Stark extraction and HPLC grade cyclohexane was used in the preparation of the reconstituted gangue, both purchased from Thermofisher Scientific Inc. The bitumen used to coat the soxhlet solids was also provided by Syncrude.

3.1.2 Dean-Stark Extraction

The Dean-Stark extraction was used to determine the content of bitumen, water, and solids in the oil sand ore sample and to obtain the soxhlet solids used in the reconstituted gangue preparation. First, 100 g of oil sand ore was weighed in an extraction thimble (Whatman™ Cellulose). Then, 150 mL of toluene was transferred to a 500 mL round-bottom flask. The thimble was hung at the top of the bottom flask using a wire holder. Following, the system was attached to a cold water condenser. Next, the flask was placed on a heater. During the process, the solvent heats, and vaporizes. The refluxed toluene dissolves the bitumen that drips and it is collected in an organic solution at the bottom of the 500 mL flask. The excess of solvent vapor, as well as the connate water, condenses in the condenser trap. As water is denser than the toluene it stands at the bottom of the trap. The system is left overnight to ensure full extraction of the toluene-soluble carbon.

The next day, the water is collected in the condenser trap and weighed. The soxhlet solids remained in the thimble are transferred to a dish to dry in the fume hood. After 2-3 hours of fume hood drying the dish is put in a vacuum oven at 70-80 °C, 25 mbar overnight. The toluene-bitumen solution is transferred to a 250 mL flash and the volume is completed with toluene up to 250 mL.

Then, triplicates of 5 mL sample are collected and slowly spread in a filter paper and previously weighed. The filter paper is hung in the fumehood to dry for 15 minutes. The difference in the weight is recorded. In the next day, the filter papers are weighed again and the final difference in the mass represents the mass of bitumen in 5 mL of organic solution. Therefore, by multiplying this value by 50 the bitumen content in the oil sand ore is obtained.

3.1.3 Soxhlet Solids Fines Separation

To reach the 10 % and 20 % fines goal in the reconstituted gangue, the soxhlet solids obtained from Dean-Stark underwent a hot wet-sieving process to separate the fine particles from the coarse solids. Figure 3.1 presents the illustrates the process based on the studies of Nikakhtari *et al.*[17] and Ikenna Ejike[32]

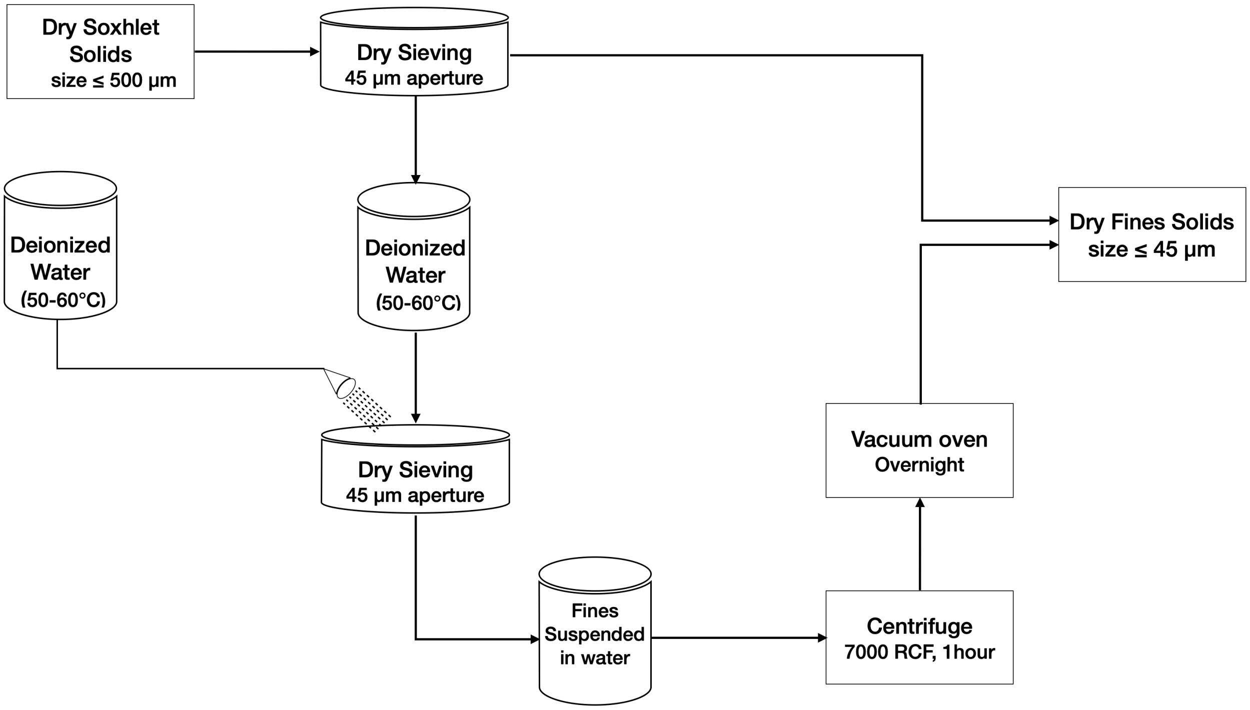


Figure 3.1: Hot water wet-sieving process to separate fines from coarse solids [17, 32].

First, the soxhlet solids obtained from the Dean-Stark (<500 μm) went through a dry sieving process for 15-20 minutes into a <45 μm sieve aperture 8" diameter sieve ASTM E-11 standard test sieve no. 325, Fisher Scientific Co., Waltham, MA. In this step, approximately 50-70 % of the total fines are separated. These fines are weighted and stored. Next, the solids greater than 45 μm were suspended in deionized water at 50-60 °C using 1-liter beaker to maximize the lumps breaking. The system is heated to 50-60 °C and mixed for 20 minutes. Following, the 1-liter fines-water suspension is poured into the <45 μm sieve aperture. The suspension is sieved for 5 minutes and liquids collected at the bottom are stored in a 2-liter plastic bucket for later use. The solids remaining in the <45 μm aperture sieve are washed with hot water and then sieved for 3-5 minutes. The process is repeated until a visually clean liquid is collected at the bottom. On average, the process required about 15-20 repeats and about 1 liter of hot water. The collected coarse solids (>45 μm) were dried in a vacuum oven at 70-80 °C, 25 mbar overnight and stored for later use.

The suspended fines samples collected in the 2-liter plastic bucket are divided into 500 mL Nalgene™ PPCO centrifuge bottles. The bottles' weights were balanced using deionized water and then centrifuged for 1 hour at 7000 RCF (relative centrifugal force) in a centrifuge Avanti J-30I (Beckman Coulter, Mississauga, ON), with JA-10 rotor (3L). The centrifuged material was dried in a vacuum oven at 70-80 °C, 25 mbar overnight and stored.

3.1.4 Particle Size Distribution

Particle size distribution analysis was performed for the fines and coarse particles obtained from the wet-sieving process. The analysis was carried out in a laser grain-size analyzer Mastersizer 3000 (Malvern Instruments, Westborough, MA), which includes measurements of laser diffraction, scattering, and backscatter [66]. The optical mode used was non-spherical mode. The Index of refraction of particles was taken from the Mastersizer in-built library for MFT particles, therefore set to 1.526. Likewise, the index of refraction of dispersant (water) was set to 1.33. The samples were prepared using approximately 1 g of solids that were dissolved in deionized water in a 20 mL glass vial. Additionally, a surfactant (sodium dodecyl sulfate) was added to the vial to allow the solids to properly disperse in the solution. The solution was treated in an ultrasonic water bath for 10 minutes to break aggregates.

The analysis initializes with background measurements, next a few drops of material was injected into the sample chamber up to approximately 5 % obscuration was observed. Following, the equipment begins the measurements while keeping a constant stirring process to avoid particles to settle.

3.1.5 Reconstituted Gangue Preparation

The Figure 3.2 illustrates the reconstituted gangue preparation based on the protocol proposed by Panda *et al.*[27]. The step-by-step process is break down in the Sections 3.1.5.2 to 3.1.5.4

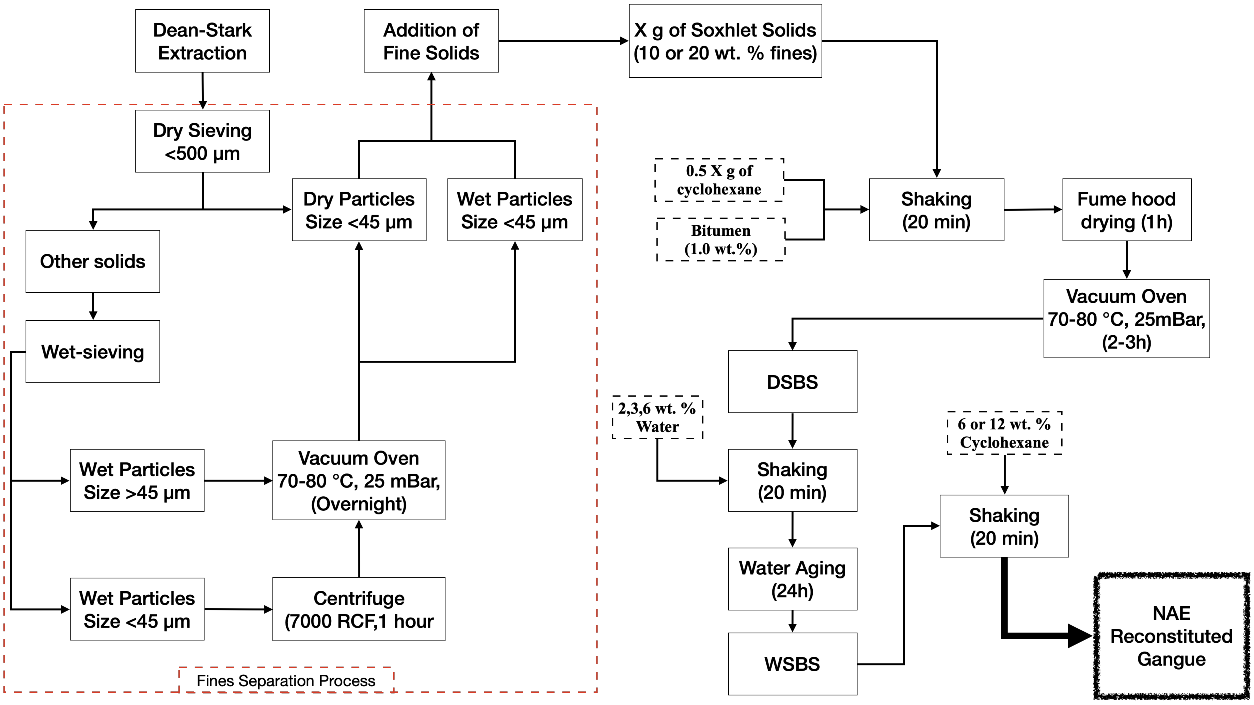


Figure 3.2: Protocol to obtain the NAE reconstituted gangue. Adapted from Panda *et al.*[27]

Triplicates were obtained for certain reconstituted gangue samples. However, it was noted that the variations in cyclohexane concentration primarily occurred from the microwave drying process, which also encompassed uncertainties related to sample handling, weighing, and packaging, rather than from the preparation of the reconstituted gangue.

3.1.5.1 Addition of Fine Solids

First, prior to the reconstituted gangue preparation the soxhlet solids dry soxhlet solids with the target fine particle fractions of 10 % or 20 % are obtained as outlined in Figure 3.3 according to Ikenna Ejike[32]. In the Figure, the target mass of fines and coarse solids are determined and weighed on a Mettler Toledo laboratory balance with an accuracy of 0.001 g a using a weighing paper. Following, the solids are placed in a 500 mL Teflon bottle and manually stirred using a spatula for three minutes. Next, the mixture was manually shaken for 20 minutes to ensure that a homogeneous mixture was obtained.

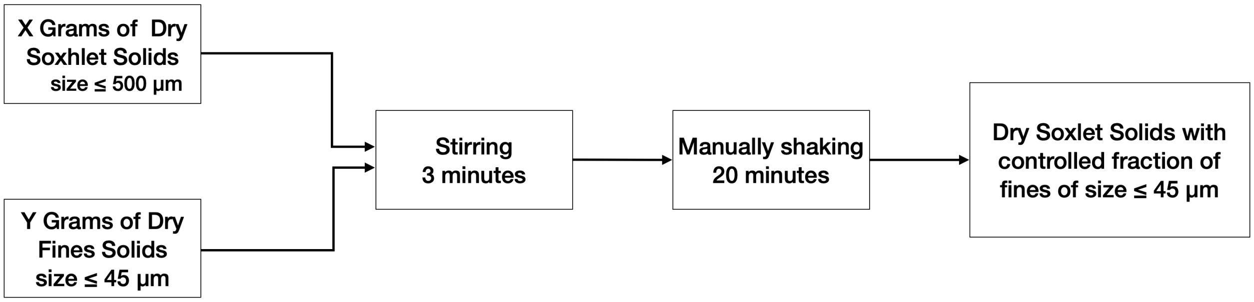


Figure 3.3: Process to obtained soxhlet solids with controlled amount of fines of size <45 µm [32].

3.1.5.2 Addition of Bitumen

The soxhlet solids obtained from the Dean-Stark are expected to be free of organic carbon due to the exhaustive toluene extraction process [27]. Therefore, bitumen is added to the soxhlet solids in order to obtain the reconstituted gangue with a controlled amount of bitumen according to the objectives discussed in Section 1.4. For this purpose, 80-150 grams of soxhlet solids with a controlled amount of fines (10 or 20 %) and an amount of half of this mass of cyclohexane were added to a 500 mL Teflon bottle according to the protocol proposed by Panda *et al.*[27]. In the next step, a mass of bitumen required to reach the 1.0 % of bitumen associated carbon was added to the mixture.

Nevertheless, bitumen is a viscous and sticky material which makes its weighing process quite challenging. To overcome this problem, first, the mass of bitumen was weighted in a petri dish. Following, a small amount of cyclohexane was added to the dish, and the mixture was stirred until the bitumen was completely dissolved. Finally, this mixture of bitumen and cyclohexane was transferred to the Teflon bottle. The mixture was stirred for 3 minutes and then manually shaken for 20 minutes. Next, the mixture was poured into a large glass dish and continuously stirred with a spatula inside a fume-hood until it is dried. This procedure was employed to ensure an even bitumen coating of the soxhlet solids as it prevented bitumen to migrate to the surface of the soxhlet solids [27].

Additionally, the glass dish with the soxhlet solids coated with bitumen was placed in the vacuum oven at 70-80 °C, 25 mbar for 2-3 hours to ensure the complete removal of cyclohexane. The last step of the process consists in taking a small sample of the solids to a CHNS elemental analysis to verify the % of bitumen carbon (Bit.C) was successfully achieved and if the bitumen was evenly distributed. The bitumen coated soxhlet solids are henceforth called Dry Soxhlet Bitumen Solids (DSBS).

3.1.5.3 Addition of Water

An amount of DSBS was weighed using a weighting paper on a Mettler Toledo laboratory balance with an accuracy of 0.001 g and then transferred to a clean 500 mL Teflon bottle. Next, the balance was tared with the weight of a 5 mL bottom-squared vial, and the proper amount of water to achieve the target of two, three or six wt% was added. Following, the required mass of water was poured into the Teflon bottle. The glass vial was reweighted to ensure that the amount of target water was transferred to the mixture. Then, the Teflon bottle was capped and sealed with Parafilm and manually shaken for 20 minutes. After shaking, the solids were left sitting for 24 hours. This water aging step was important to allow the water to enter into the pores of the DSBS solids. The product, called Wet-Soxhlet Bitumen Solids (WSBS), was kept within the Teflon bottled capped and Parafilm sealed to prevent water loss. According to Panda *et al.*[27], the calculated weight of water is based on the DSBS and WSBS weights instead of the weight of the final reconstituted gangue.

3.1.5.4 Addition of Cyclohexane

Nikakhtari *et al.*[17] performed non-aqueous extraction employing different solvents. They observed an average value of 18 wt% solvent in the gangue before the drying process. Renaud[65] studied the effects pressure and temperature on the removal of cyclohexane fom gangue obtained from a NAE, it was found out that the initial cyclohexane concentration after the NAE has taken place varies from 8 to 18%. Ikenna Ejike[32] found a mean value of 12 % for the cyclohexane content prior to drying. Previous works that studied the recovery of cyclohexane from the gangue mainly applied the fixed value of 12 % of cyclohexane. Therefore, 6 wt% and 12 wt% concentration of cyclohexane was selected to perform the microwave heating drying experiments.

The addition of cyclohexane is the last step to obtain the final NAE reconstituted gangue. First, the balance was tared with the weight of a 5 mL bottom-squared vial, and the proper amount of cyclohexane to achieve the target of 6 or 12 wt% was added. Following, the mass of cyclohexane was poured into the Teflon bottle containing the WSBS previously obtained. The glass vial was reweighted to ensure that the amount of target cyclohexane was transferred to the mixture. Then, the Teflon bottle was capped and sealed with Parafilm and manually shaken for 20 minutes. After the mixing, the reconstituted gangue was obtained. The samples were stored in a freezer at -13 °C to minimize the solvent loss.

3.2 CHNS Elemental Analysis

The carbon content in the soxhlet solids and in the DSBS samples was determined using a carbon, hydrogen, nitrogen, and sulfur elemental analysis equipment also known as a CHNS analysis. In other words, the CHNS analysis was employed to verify the bitumen content added during the reconstituted gangue preparation process. The equipment used was a Flash 2000 CHNS/0 Analyzer, Thermo Scientific. First, a void tin sample, and 5 triplicates of 12-14 mg of a soil reference with known concentrations of carbon, hydrogen, nitrogen, and sulfur were loaded into the autosampler. The empty tin was used as a blank and the 5 triplicates to build a calibration curve for the analysis. Then, small samples of 12-14 mg homogenized using a mortar and a pestle were weighed in tin capsules. Then, these capsules were carefully closed and loaded into the equipment autosampler. A total of five triplicates were loaded per sample tested. Once the analysis started, the autosampler sent the samples to a quartz combustion reactor found within a furnace set to a temperature of 900 °C. The reactor is an extremely oxidizing environment that triggers a strongly exothermic reaction that can reach temperatures as high as 1800 °C which causes an instant combustion of the sample. A complete oxidation was completed within the reactor, nitrogen oxides and sulfur trioxides that potentially can be formed were reduced to nitrogen and sulfur dioxides. Next, CO_2, N_2, H_2O, and SO_2 gases from the reactions were separated by a chromatography column. The eluting gases from the chromatography column went through a thermal conductivity detector (TCD). The electrical signals created by the TCD were processed by Eager Xperience software. The percentages of carbon, hydrogen, nitrogen, and sulfur in the sample were therefore obtained.

3.3 Microwave setup

Microwave heating experiments were conducted in a Laboratory scale microwave setup consisting of a microwave generator (MH2.0W-S, National Electronics) equipped with 2.45 GHz magnetron, a 2 kW switch-mode power supply (SM745G.1, Alter), a three-stub tuner (National Electronics), a single mode waveguide applicator, and a sliding short. The microwave power was monitored with a dual channel microwave power meter (E4419B, Agilent), two power sensors (8481A, Agilent), and a dual directional coupler with 60 db attenuation (Mega Industries). Applied power was maintained at (230 ± 1) W throughout the experiments. A fiber optic temperature sensor with a signal conditioner (Reflex signal conditioner, Neoptix) was used to monitor the temperature of the sample during the microwave heating. Temperature, forward power was read over the time with a Lab View program (National Instruments). A air flowing at a rate of 0.50 standard liters per minute (SLPM) was employed to purge the evaporated mixture of cyclohexane and water from the vial.

The dielectric constant ε' and the dielectric loss ε'' for cyclohexane [52] as well as for oilsand ore [67] are very low. Hence, as observed by Khalkhali *et al.*[28] neither the cyclohexane nor soxhlet solids were heated by microwaves. Therefore, this work follows the methodology discussed in the literature [28, 58, 68] of adding water as susceptor of microwave of the energy on remediation of contaminated solid with organic compounds. This methodology was successfully implemented by Khalkhali *et al.*[28] to regenerate cyclohexane from a oilsand ore soxhlet solids sample.

3.4 Microwave Drying Process

Gangue samples with cyclohexane and water concentrations according to the discussion in the Section 1.4 were dried in the microwave setup for 780 seconds. The lowest water-cyclohexane ratio capable to reduce the cyclohexane concentration to levels below 250 ppm in all samples was used to build the drying rate curves.

First, triplicate samples of reconstituted gangue, weighting (5008 ± 107) mg are transferred straight to a clear borosilicate glass vial (DWK Life Sciences, 5.5 mL, 19 OD x 40

H mm). The mean value was determined based on data obtained from three triplicates of 24 unique samples . The samples's weight were obtained using a Mettler Toledo laboratory balance with an accuracy of 0.001 g. The packing was kept at a height of 15 mm to provide consistent MW heating throughout the samples. After the microwave drying, HPLC toluene was used to extract the cyclohexane from the dried gangue sample as successfully performed by Khalkhali *et al.*[28]. In this extraction process, first, the sample is transferred to a glass centrifuge glass tube (Kimble 50 mL borosilicate glass 5.1). Next, approximately 10g of toluene is added to the tube and then manually shaken for 20 minutes. After 24 hours 5g of the supernatant is collected. Then, 1 mL of the supernatant goes through a filtration process utilizing a nylon filter media, pore size of 0.2 μm filter 13mm diameter (Whatman Puradisc 13). Finally, 100 mg of the supernatant is weighted in a 2 mL headspace chromatography vial (PTFE/silicone septa), along with 10 μL of internal standard methyl cyclopentane. The vial is filled with methylene chloride up to 1.5 ml. All the weights are noted to further determination of the concentration of cyclohexane in the vial, the toluene-cyclohexane sample, and then the gangue sample. These steps were repeated up to 3 times as needed [28]. Typically, a two-step extraction process was enough for most samples, however, samples with high residual concentrations of cyclohexane required a third step. Figure 3.4 illustrates the method [28].

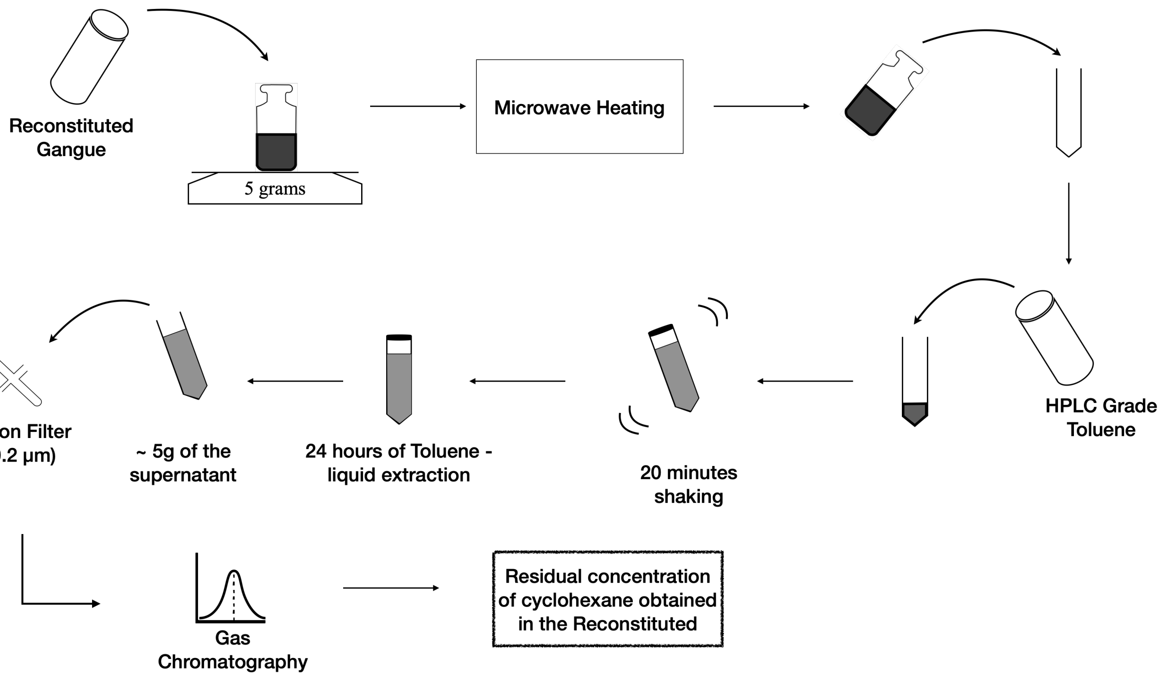


Figure 3.4: Liquid- extraction of residual cyclohexane from reconstituted gangue samples

3.5 Gas Chromatography

3.5.1 Apparatus

After extraction with toluene, the residual cyclohexane analysis was carried out with Trace GC Ultra coupling DSQ II Single Quadrupole MS, ThermoFisher (Scientific, Waltham, MA, USA). The injections were performed by an AI3000 auto-injector autosampler attached to the GC-MS equipment. The separation was performed on a Thermo TR-5 column (nonpolar phase, 5 % phenyl methyl polysiloxane) 30 m in length, 0.32 mm inner diameter, and 0.25 μm film thickness. High-purity helium (Praxair, Canada) was used as the carrier gas. Air at a flow rate of 350 mL/min was used as a source of oxygen, and high-purity hydrogen at 35 mL/min as a fuel source.

To make the standards for the calibration curve methylene chloride ultra-trace analysis was used and purchased from Fisher Scientific International. Cyclohexane and toluene HPLC grade were supplied by Thermo Fisher Scientific, and methyl cyclopentane was 97 % pure by Sigma-Aldrich.

3.5.2 Selection Of The Gas Chromatography Solvent

Table 3.1 shows the gas chromatography solvents and their respective normal boiling points. Methylene chloride has the lowest normal boiling point in the group of tested solvents, therefore the elution time was the shortest providing an excellent separation from the internal standard (methylcyclopentane) and the analyte (cyclohexane). Further, it was noticed that solvents with higher boiling points may contain heavier contaminants that can cause more polluted chromatograms reducing the chromatographic resolution.

Table 3.1: Gas chromatography solvents tested.

Solvent	**Normal Boiling Point °C**
Methylene Chloride	39.8
n-hexane	68.7
Toluene	110.6

3.5.3 Selection of the Internal Standard

The selection of an internal standard is based on the properties of the analyte such as boiling point, polarity, and chemical structure. Additionally, the internal standard must have a reasonable difference in retention times from the analyte [69]. Table 3.2 shows the chemicals tested.

Methylcyclopentane revealed the best chromatographic resolution for both the solvent and the analyte. Figure 3.5 shows the chromatogram obtained for the mixture. The first peak shows at 2.7 minutes and corresponds to the elution of the solvent methylene chloride. Next, at 3.6 seconds the elution of the internal standard methyl cyclopentane, following the cyclohexane peak at 4.2 minutes, and lastly the toluene at 5.6 minutes.

3.5.4 Sample Preparation

Duplicate samples were diluted in a 1:20 ratio in methylene chloride prior to injection. A 10 μL syringe was used in the autosampler, which was programmed to rinse 3 times with

Table 3.2: Internal standards tested for gas chromatography.

Solvent	**Normal Boiling Point °C**
2,2-Dimethylbutane [69]	50
1-butanol [70]	117.7
n-hexane[71]	68.7
n-heptane[71]	98.4
methylcyclohexane[71]	101
3-methylpentane	63
2-methylpentane	60
2,3-Dimethylbutane	58
cyclopentane	49.2
methyl-cyclopentane	71.8

methylene chloride before and after each injection. The carrier gas flow rate was set at a flow rate of 1.0 mL/min throughout the runs.

In an analytical method, determining the limit of detection (LOD) and limit of quantification (LOQ) is an important part of the analytical method [72]. The LOD provides the minimum analyte concentration that can be detected by the method, however not necessarily reliable [72]. In a sense, the LOD is the minimum concentration of analyte that is distinguishable from the blank noise. The LOQ refers to the lowest analyte concentration at which the concentration of the analyte is obtained with acceptable accuracy [72]. This work followed the signal-to-noise method to obtain LOD and LOQ. In this method, a signal-to-noise ratio of 3:1 between the analyte signal and the mean of the blank noise determines the method's limit of detection (LOD) [72]. Similarly, a ratio of 10:1 is applied to obtain the limit of quantification (LOQ) [72].

Upon measurements of signal-to-noise in several chromatograms, it was observed that the concentration in the wet gangue at which the signal-to-noise ratio is 3:1 and 10:1 is 45 ppm and 150 ppm, respectively. Thus, the concentration of the residual cyclohexane for any

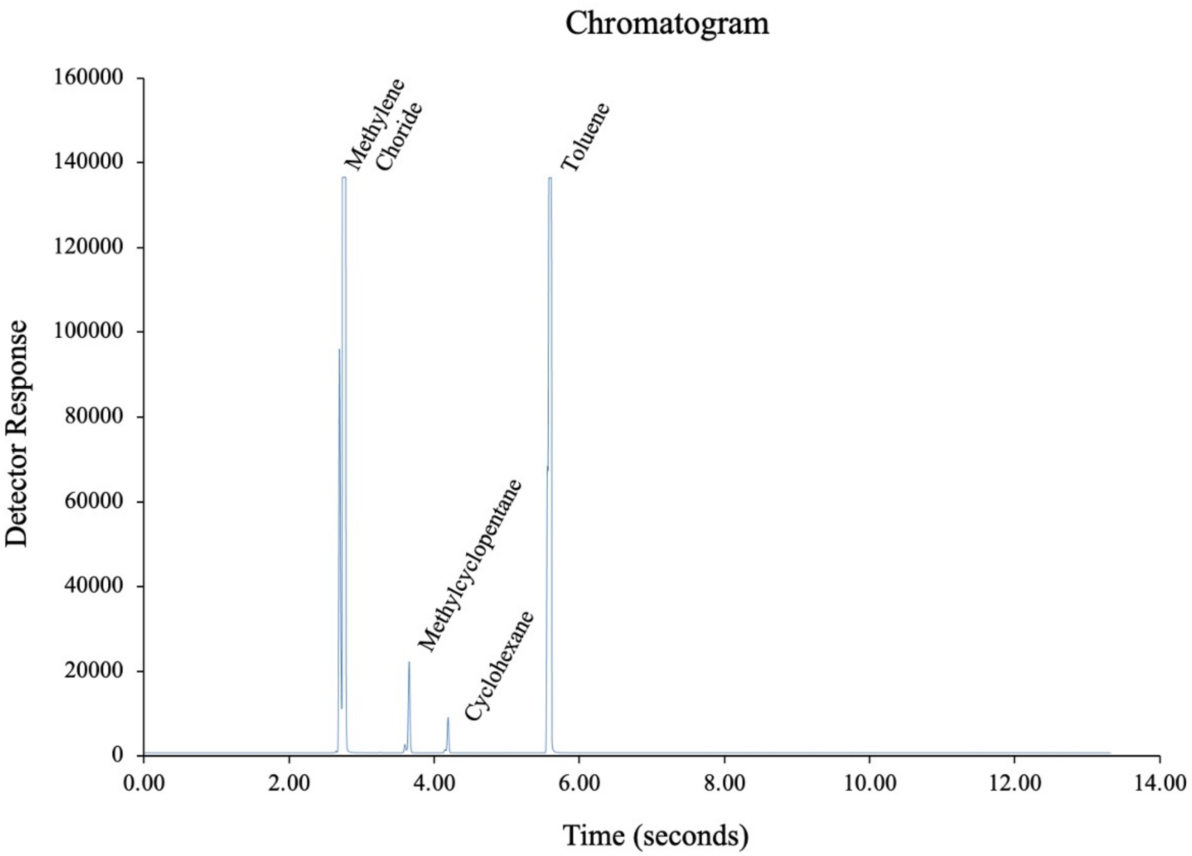


Figure 3.5: Typical chromatogram observed for the mixture of toluene, cyclohexane, and methylcyclopentane dissolved in methylene chloride

sample that would exhibit a signal at which the concentration of cyclohexane below 150 ppm is hereby referred ”not-detected”.

3.5.5 Calibration Curve

Following the sample preparation method described in the previous section, a calibration curve was built based on five known concentrations of cyclohexane in toluene of approximately 75, 150, 1,500, 15,000, and 150,000 ppm. A chart plot of the ratio the cyclohexane response to the internal standard against the ratio of the known concentration of cyclohexane over the internal standard. Therefore, a linear model can be obtained as shown in the Equation 3.1

$$\frac{R_{CH}}{R_{IS}} = \frac{C_{CH}}{C_{IS}}K \tag{3.1}$$

Where R_{CH} and R_{IS} are the detector response (peak area) obtained for the cyclohexane and internal standard, respectively. The concentration of cyclohexane and the internal standard are represented by C_{CH} and C_{IS}.

In the curve, the x-axis is the ratio of concentration of cyclohexane over concentration of internal standard, and the y-axis the peak area obtained for cyclohexane divided by the peak area of internal standard. Therefore, a linear correlation between the concentration of cyclohexane, the concentration of internal standard, and the detector response can be expressed by the Equation 3.2

$$C_{CH} = \frac{R_{CH}}{R_{IS}} \frac{C_{IS}}{K} \tag{3.2}$$

Figure 3.6 illustrates the calibration curve obtained. The experimental data points show an excellent agreement with a linear model (R^2 =1.00), and the Equation 3.3 shows the calibration curve model:

$$C_{CH} = \frac{R_{CH}}{R_{IS}} \frac{C_{IS}}{0.94} \tag{3.3}$$

Additionally, control samples were used to account for oscillations of the detector response. In this manner, two standard samples with concentrations of cyclohexane close to the NAE gangue assessed were prepared. These samples were injected before the NAE samples in order to obtain an updated response factor (K). The updated response factor was used to determine the cyclohexane concentration in the NAE gangue under assessment.

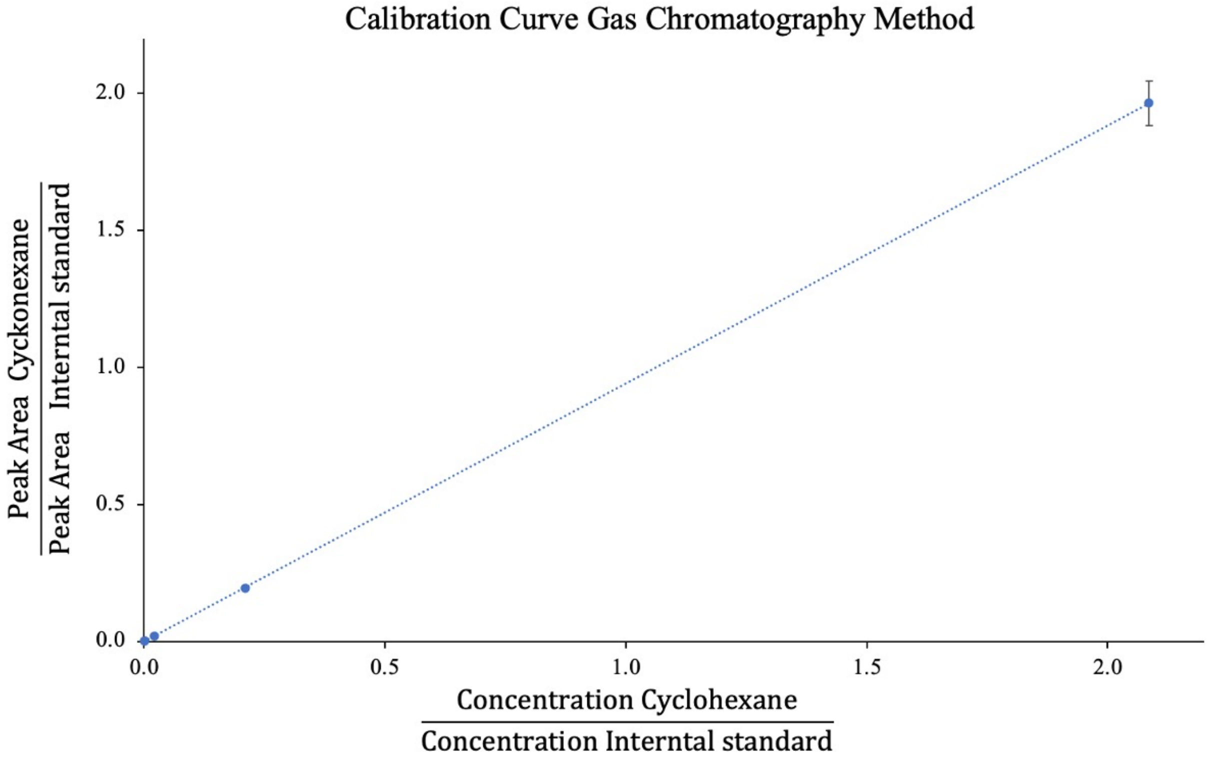


Figure 3.6: Gas chromatography calibration curve

4. Results and Discussions

4.1 Oil Sands Ore Characteristics

As discussed in Section 3.1.2, a Dean-Stark extraction was performed to obtain the soxhlet solids and to characterize the properties of the oil sand ore. Table 4.1 provides the results based on 8 complete extractions and wet-sieving processes for the contents of bitumen, water, fines, and coarse solids for the rich-grade ore used in this study.

Table 4.1: Characteristics of the rich-grade oil sand ore

Bitumen[1]	**Water**[1]	**Fine Solids (<45 μm)**[2]	**Total Solids**[1]
(12.0 ± 0.7) wt%	(1.2 ± 0.2) wt%	(5.8± 0.4) wt%	(85.8 ± 0.5) wt%

[1] wt% based on the total oil sand ore weight.
[2] wt% based on dry solids only.

The results obtained for bitumen, water, and fine samples are in the range expected for a high-grade ore sample according to the previous literature [2, 25, 27, 28, 73]

4.2 CHNS Elemental Analysis Results

The CHNS analysis was performed in samples prior to and after adding bitumen to the soxhlet solids. As discussed in Section 3.1.5.2, the exhaustive toluene extraction process the remaining carbon in the soxhlet solids after the Dean-Stark extraction is of inorganic nature. Therefore, by measuring the carbon fraction in the soxhlet solids and the DSBS solids it is possible to confirm whether the target concentration of Bit.C in the DSBS was successfully achieved.

Table 4.2: Results for CHNS elemental analysis.

Sample	**Solvent used in the Dean-Stark**	**Carbon (wt%)**	**Bitumen (wt%)**
Sohlet solids	Cyclohexane	(0.40 ± 0.02) n=10	0
DSBS	Cyclohexane	(1.43 ± 0.02) n=10	(1.03 ± 0.04) n=10
Sohlet solids low fines	Toluene	(0.17 ± 0.02) n=10	0
DSBS low fines	Toluene	(1.22 ± 0.07) n=10	(1.05 ± 0.08) n=10
Sohlet solids high fines	Toluene	(0.29 ± 0.02) n=5	0
DSBS high fines	Toluene	(1.43 ± 0.04) n=5	(1.14 ± 0.07) n=5

Table 4.2 shows the results obtained for soxhlet solids and DSBS solids for samples containing low and high fines fractions using toluene and cyclohexane as a solvent. A total of five replicates (n=5) were performed for each sample. According to the results, the soxhlet solids obtained from Dean-Stark extraction using cyclohexane as a solvent revealed a higher residual carbon than when toluene was used. Khalkhali and Choi[25] observed higher carbon content in fine particles rather than coarse solids for soxhlet solids obtained from Dean-Stark using cyclohexane as a solvent. Besides the fact that fines have a higher specific surface area, asphaltenes precipitate on the surface of fine particles when cyclohexane is used as an extracting solvent [74].

According to the results, toluene was able to provide cleaner soxhlet solids than cyclohexane. Therefore, as the samples were further submitted to a liquid extraction with toluene after the microwave drying toluene was selected as a solvent for the Dean-Stark extraction. Additionally, the average of bitumen carbon obtained for DSBS solids for both low and high fines contents was (1.08 ± 0.08) wt% (n=15). Thus, the target of 1.0 wt% bitumen carbon in the reconstituted gangue was successfully achieved with a deviation below 10 % around the average.

Moreover, soxhlet solids with higher fines content exhibited higher fractions of toluene-insoluble organic carbon. This result was expected as fine particles < 45 μm are higher in toluene-insoluble carbon [32, 75]. Furthermore, the samples with higher fine fractions exhibited a better performance in the bitumen coating process. This was attributed to the fact the fine particles have a higher specific surface area compared to the coarse solids.

4.3 Particle Size Distribution

As observed in Table 4.3, in the sample containing the isolated fines, 90 % of the fine particles have a size below 53 μm. In the isolated coarse sample, only 10 % show sizes below 140 μm. Additionally, the data show that the minimum size detected for the all fines sample was 0.405 μm (0.12 % volume) and only 1.2 % were greater than 100 μm. For the all coarse sample, 86.4 μm (0.09 %) was the minimum size detected and 586 μm (0.06 %) the maximum. Therefore, the hot water wet-sieving process described in the section 3.1 utilized to separate the fines from the oilsand ore soxhlet solids was satisfactory. Thus, 10 and 20 % of fines reconstituted gangue samples were adequately obtained.

Figure 4.1 shows the particle size distribution for each sample.

Table 4.3: Particle size distribution

Sample	**Dx (10) (μm)**	**Dx (50) (μm)**	**Dx (90) (μm)**
Fine solids	3.07 ± 0.01	19.4 ± 0.1	53.4 ± 1.2
Coarse solids	140.0 ± 0.2	202.0 ± 0.4	317 ± 1

Figure 4.2 shows samples of isolated fines and isolated coarse solids obtained after the wet-sieving process discussed in Section 3.1.3. As observed in Figure 4.2a, the isolated fines are darker than the coarse solids, which was expected due to the higher carbon content in fine particles [25, 74].

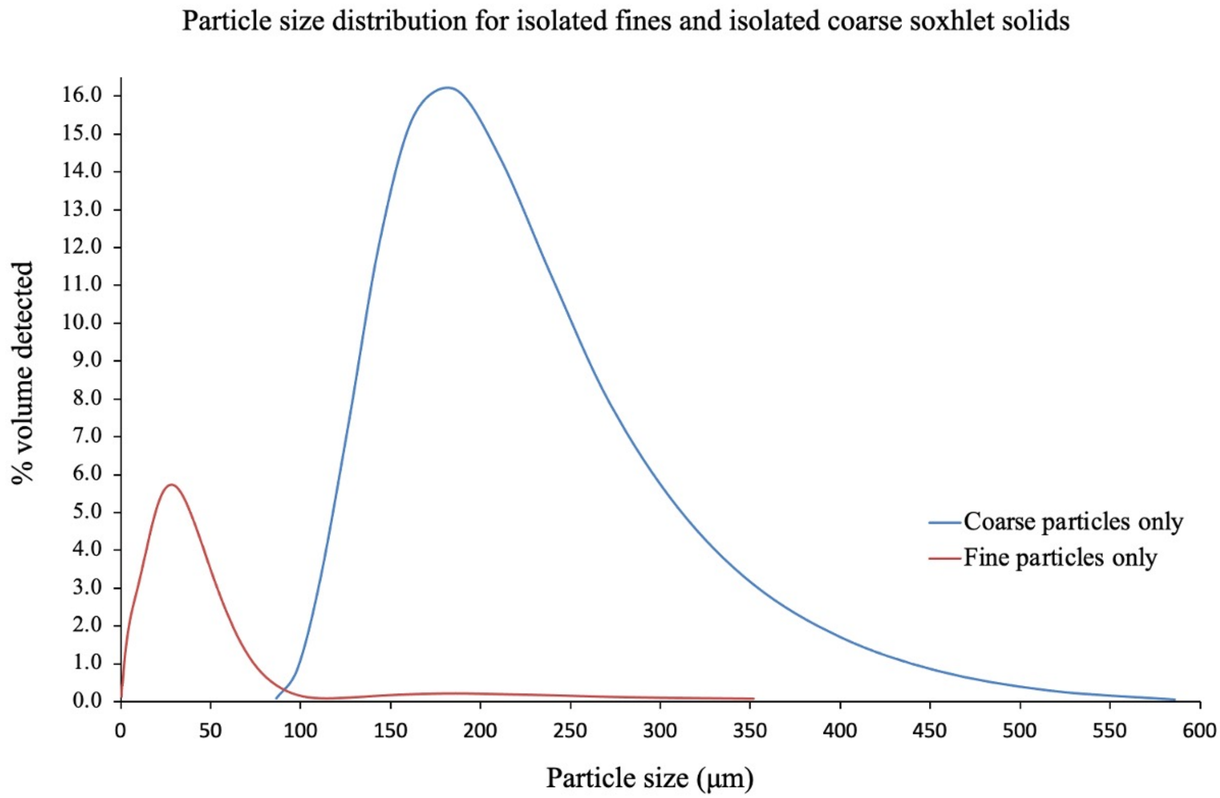
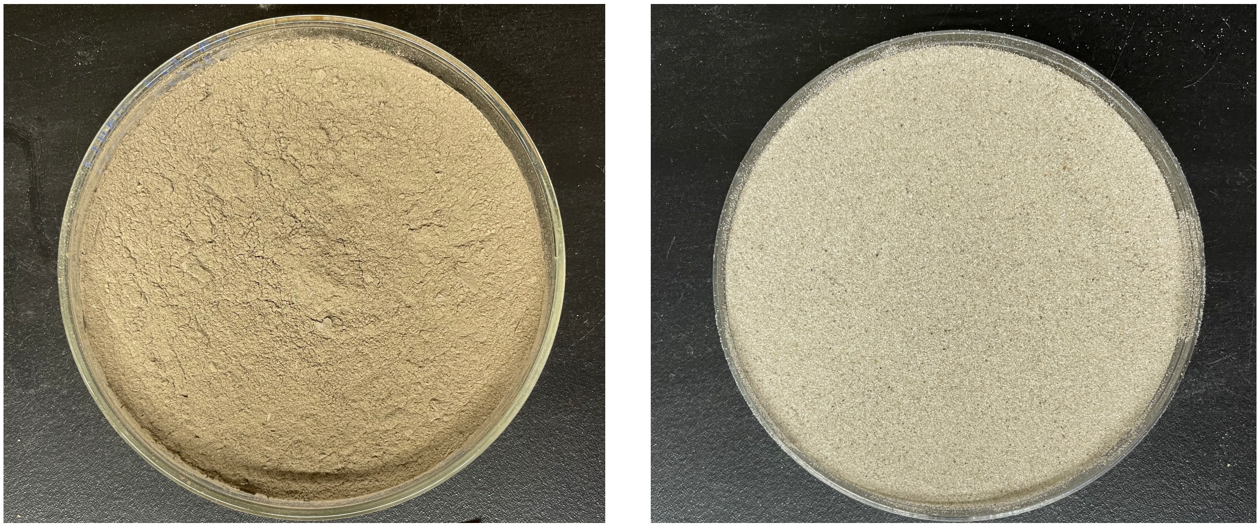


Figure 4.1: Particle size distribution for isolated fines and isolated coarse solids obtained from Athabasca oilsand ore soxhlet solids obtained



(a) Isoleted fine particles

(b) Isolated coarse particles

Figure 4.2: Isolated fines and coarse particles obtained from wet-sieving process.

4.4 Temperature Profile Microwave Heating

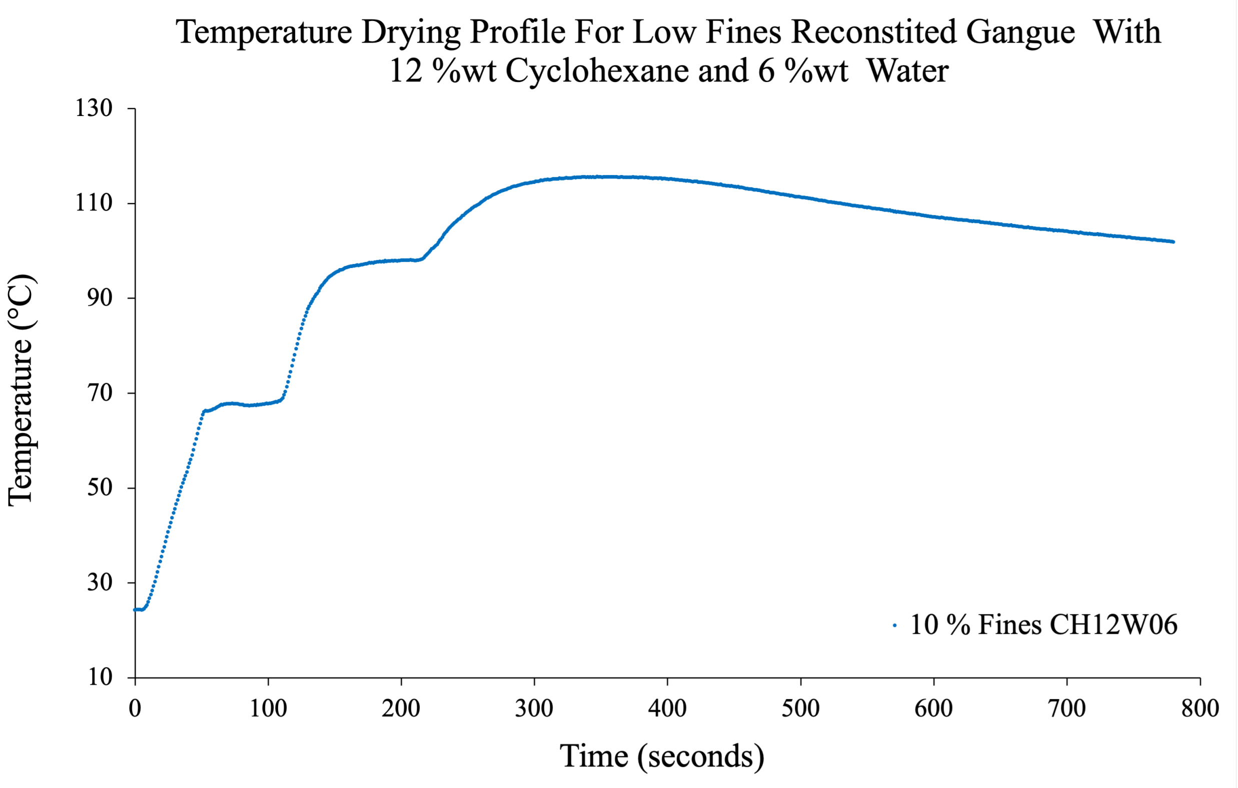
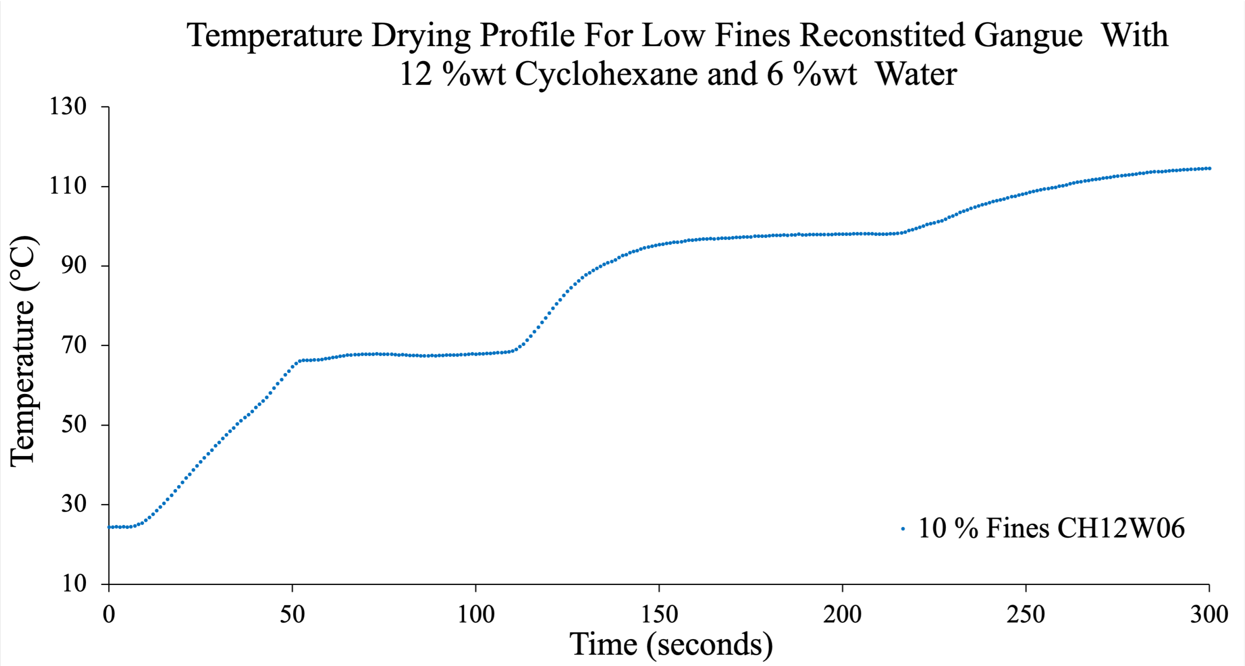


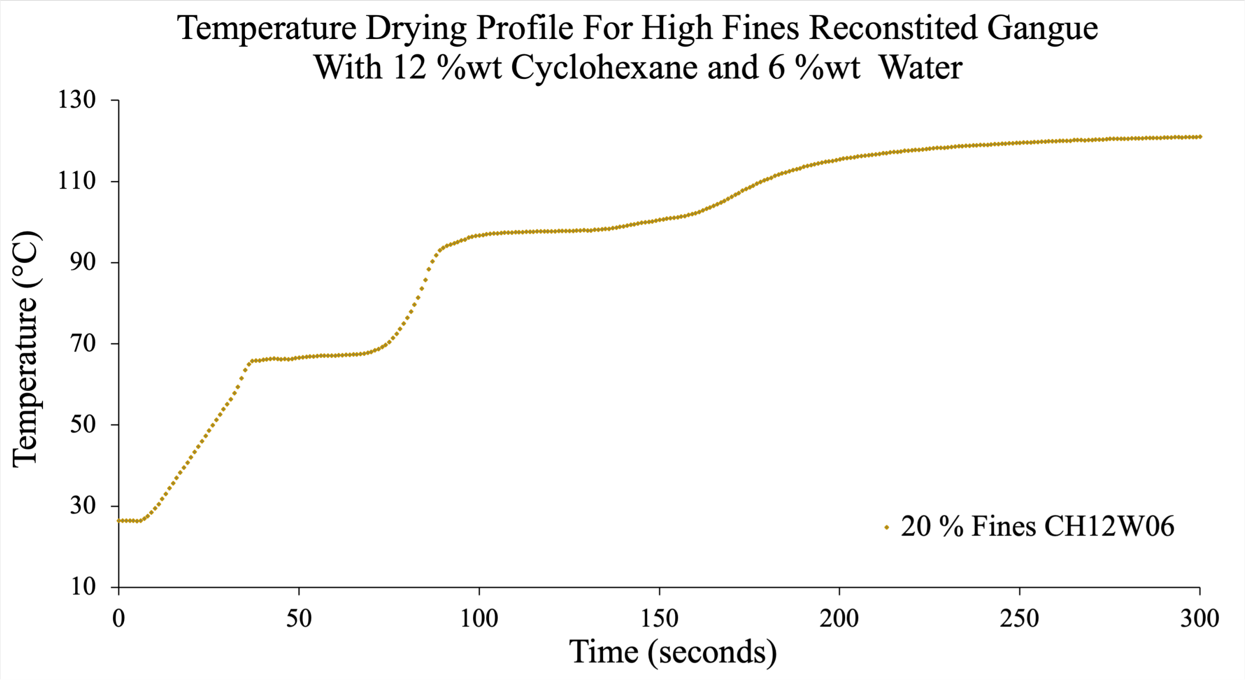
Figure 4.3: Temperature profile of microwave heating of low fines NAE reconstituted gangue with 12 wt% cyclohexane and 6 wt% water (solvent-free basis)

Figure 4.3 shows a typical temperature profile for drying reconstituted gangue applying microwave heating over a period of 780 seconds of drying. The sample is vigorously agitated during the reconstituted gangue preparation, thus the concentrations of water, cyclohexane, and solids (fines and coarse) are assumed to be homogenously distributed throughout the sample. According to the Figure, there are three temperature plateaus in the profile, one at approximately 68 °C, another at approximately 98 °C, and one at approximately 115 °C. The first plateau of drying can be interpreted as the vaporization of cyclohexane, the second as the vaporization of water, and the third as the upper limit of temperature the system can achieve before the temperature begins to decrease. [28]. The normal boiling point of bulk cyclohexane is 80.75 °C at 101325 Pa. Nonetheless, Khalkhali *et al.*[28] discuss that as water and cyclohexane are immiscible, cyclohexane's activity increases in the presence of water, which explains a drop in the cyclohexane boiling point. Moreover, the immiscibility effect did not impact the water as by the time the system reaches the water boiling point, the majority of the cyclohexane has already evaporated. Therefore, the plateau for the vaporization of water, however, is observed to be approximately 98 °C, which is expected considering the elevation where the experiments were carried out (645 m above sea level). However, as discussed in Section 2.2.2 previous studies of MWH of contaminated soils typically report recorded soil bulk temperature below the boiling point of the contaminants [28, 45, 46, 76], and this behaviour might be attributed to the selective nature of the MWH [29].

Likewise, Figure 4.4 contrasts the temperature profile for samples containing 12 wt% cyclohexane and 6 wt% water for low fines (Figure 4.4a) and high fines content (Figure 4.4b). For a better visuazation of the results the chart displays the first 300 seconds of microwave heating. The plateaus occur at the same temperature, however, they are observed to be shorter. Additionally, it was observed that the slope of temperature increase is steeper for samples with higher fine particles content. Fine particles show a specific surface area significantly larger than the coarse solids, for example, clay particles (<4 μm) exhibit a specific surface area up to 10 times higher than medium sand ($200-300$ μm) [77]. Therefore, adding fines in the reconstituted gangue samples is expected to increase the contact area between the MW susceptor (water) and the sample. Thus, improving the energy transfer efficiency between the water and the cyclohexane in gangue samples with higher fines content.



(a) Low fines reconstituted gangue with 12 wt% cyclohexane and 6 wt% water .



(b) High fines reconstituted gangue with 12 wt% cyclohexane and 6 wt% water

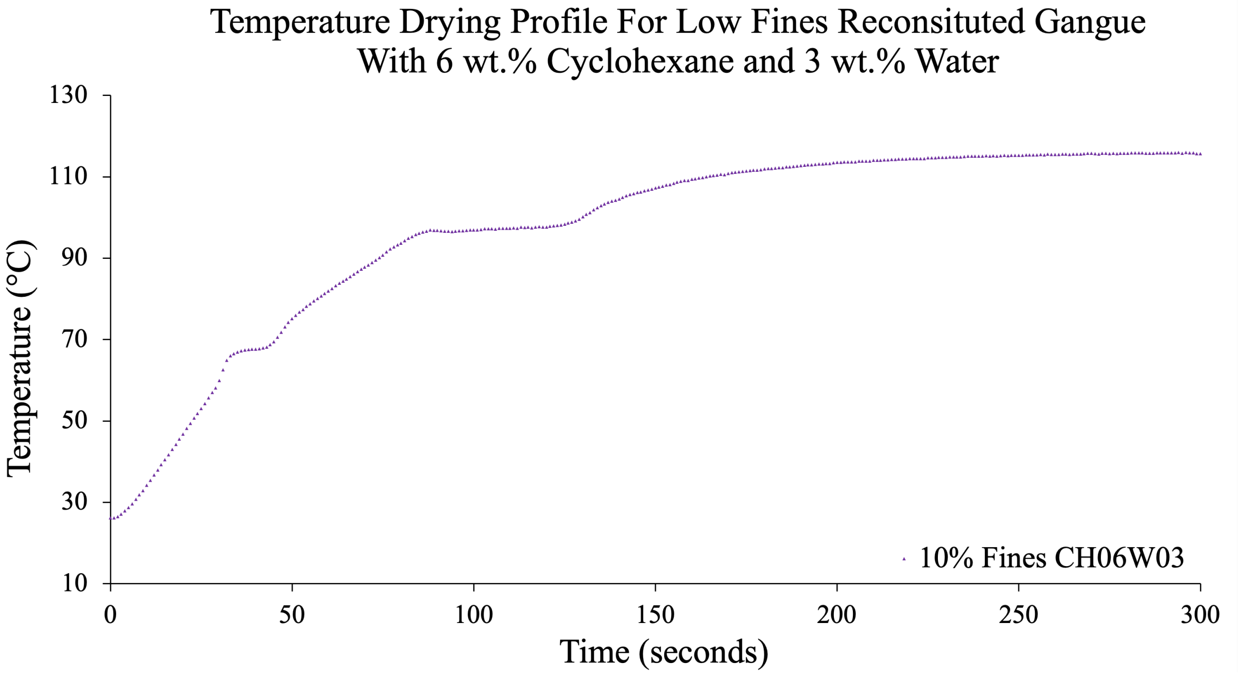
Figure 4.4: Temperature profile for low and high fines samples of NAE reconstituted gangue containing initial 12 wt% cyclohexane and 6 wt% water .

Similarly, Figure 4.5 shows the temperature profile for high and low fines samples for an initial concentration of cyclohexane of 6 wt% and 3 % wt. water. The charts follow the same trend observed for 12 % cyclohexane, one at approximately 68 °C and another at 98 °C. Additionally, even though in a small magnitude, the sample with higher fines content also exhibited a shorter plateau for cyclohexane and a steeper temperature increase slope.

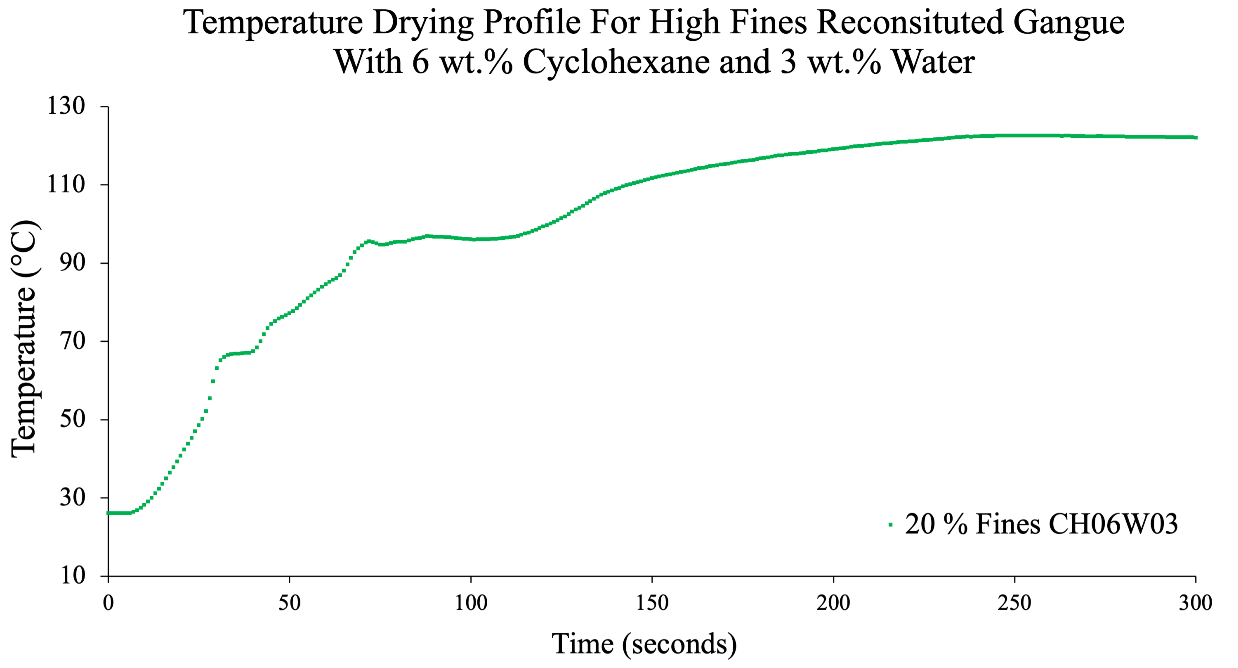
Figure 4.6 displays the temperature profile for low fines content containing initial 12 % and 6 % cyclohexane. The temperature profiles for these initial concentrations but with high fines content samples are displayed in Figure 4.7. Comparing the samples with the same fine content but different initial cyclohexane concentrations, samples with lower cyclohexane content exhibited shorter plateaus. The plateaus characterize the phase transition from liquid to vapor, therefore as the concentration of cyclohexane in the gangue is reduced, the plateaus are expected to decrease. Nonetheless, the reduction observed was not linear. The same non-linear behavior was observed in the drying rate curves as further discussed in Section 4.5.

In addition, it is interesting to note that samples with the same fine content but lower initial cyclohexane concentration exhibited a steeper slope for the initial temperature increase. There are two points to note about this. First, cyclohexane has a low specific heat, which means it requires a low energy input per unit of mass to increase its temperature. Therefore, the heat that the cyclohexane absorbs from the microwave susceptor is readily converted into sensible heat increasing the system temperature. Additionally, as the specific heat is a function of the mass, the lower the mass of cyclohexane the lower the energy required to observe the same temperature increase. These two factors contribute to observing a higher first slope of temperature in samples with a smaller initial concentration of cyclohexane. Conversely, samples with low initial cyclohexane concentration (6 % cyclohexane and 3 % water) exhibited a less steep slope for the second temperature increase compared to samples with higher initial cyclohexane concentration (12 % cyclohexane and 6 % water). In this case, the concentration of the microwave susceptor (water) was demonstrated to be the primary factor contributing to the increase in the system temperature during the second slope.

Additionally, reconstituted gangue samples contaminated with cyclohexane only did not demonstrate a significant temperature rise when exposed to microwaves. This observation validates the limited ability of both the solids and cyclohexane to absorb microwave energy [28]. It also supports the idea that employing water as a microwave susceptor is an effective strategy, as previously noted by Khalkhali *et al.*[28]. Lastly, the temperatures were recorded every second which made it ineffective to present the error bars for the average temperature.

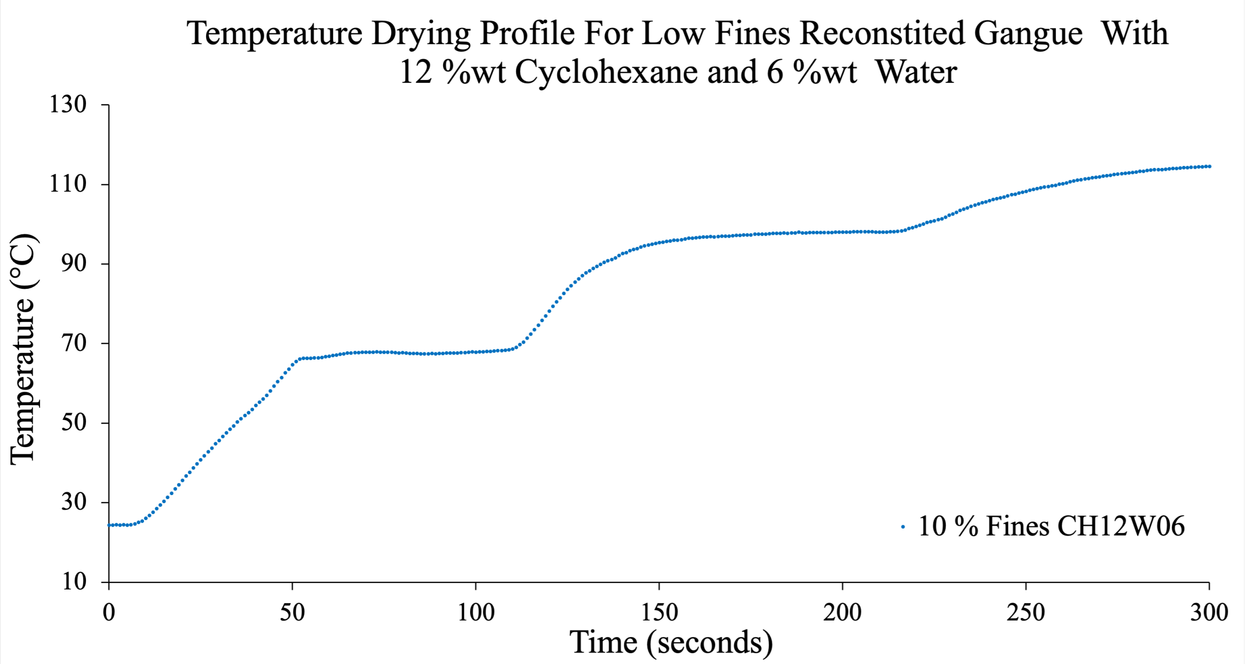


(a) Low fines reconstituted gangue with 6 wt% cyclohexane and 3 wt% water.

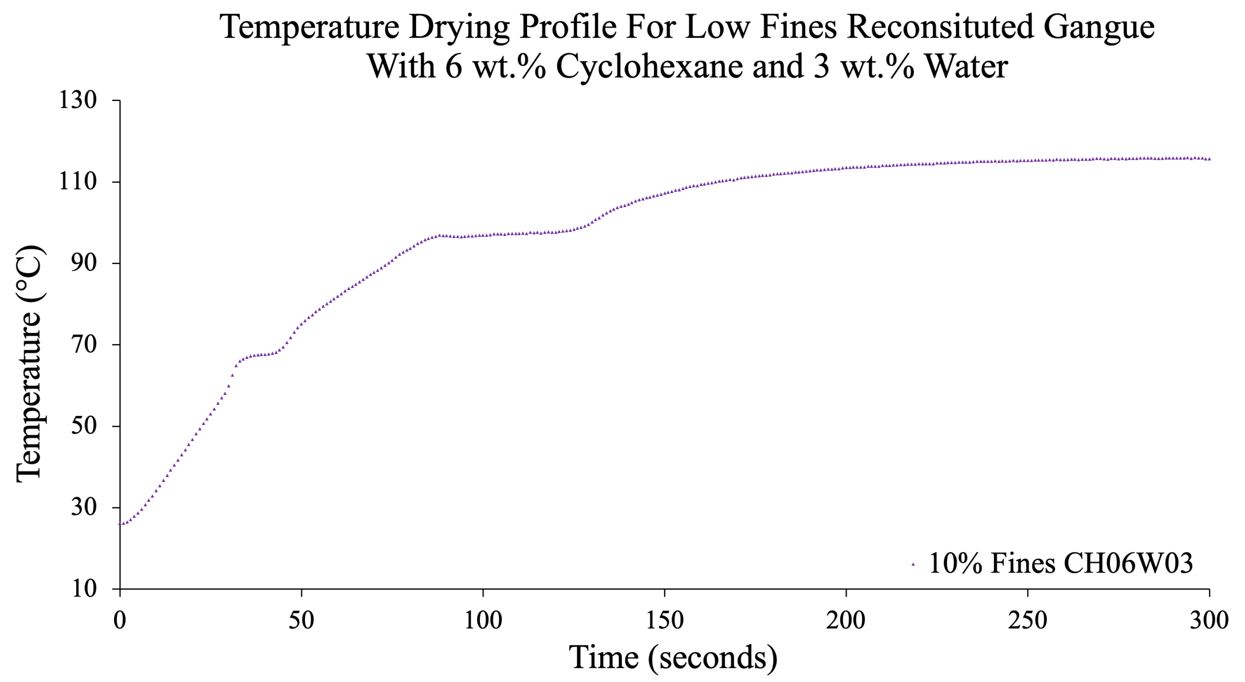


(b) High fines reconstituted gangue with 6 wt% cyclohexane and 3% water.

Figure 4.5: Temperature profile for low and high fines samples of NAE reconstituted gangue containing initial 6 wt% cyclohexane and 3 wt% water.

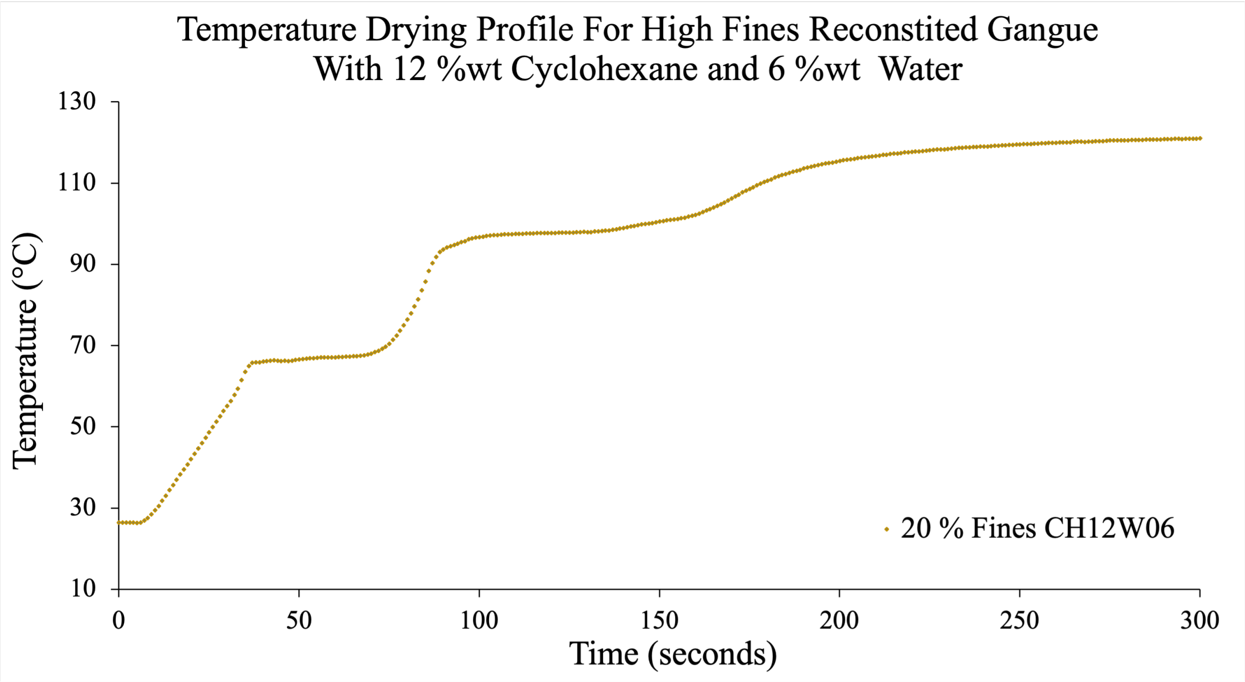


(a) Low fines reconstituted gangue with 12 wt% cyclohexane and 6 wt% water.

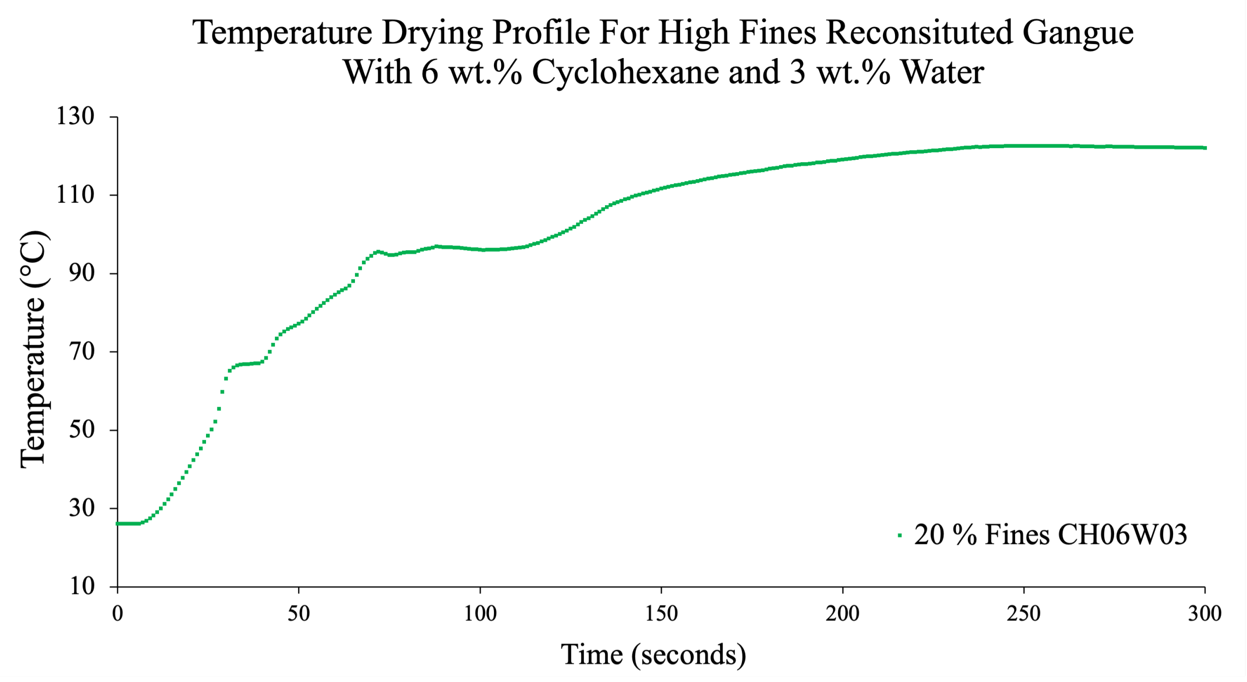


(b) Low fines reconstituted gangue with 6 wt% cyclohexane and 3% water.

Figure 4.6: Temperature profile for low fines samples of NAE reconstituted gangue containing initial 12 wt% cyclohexane and 6 wt% water and for 6 wt% cyclohexane and 3 wt% water.



(a) High fines reconstituted gangue with 12 wt% cyclohexane and 6 wt% water.



(b) High fines reconstituted gangue with 6 wt% cyclohexane and 3% water.

Figure 4.7: Temperature profile for high fines samples of NAE reconstituted gangue containing initial 12 wt% cyclohexane and 6 wt% water and for 6 % Cyclohexane and 3% water.

4.4.1 Maximum Temperature Achieved during the Microwave Heating

Table 4.4 shows the maximum temperature observed at each sample.

Table 4.4: Maximum temperature.

Sample	**Maximum Temperature**
CH06_W03_10F	(112 ± 6) °C
CH12_W06_10F	(115 ± 3) °C
CH06_W03_20F	(118 ± 6) °C
CH12_W06_20F	(125 ± 7) °C

The system reached the maximum temperature of ranging approximately from 112 to 125 °C, a temperature above the normal boiling point of the water, as observed by Khalkhali *et al.*[28] and Robinson *et al.*[47]. Khalkhali *et al.*[28] suggest that the overheating temperature of the water (microwave heating agent) may be due to the further heating of the water vapor within the gangue before leaving the solid. Nonetheless, as discussed in the Section 2.2.1 Robinson *et al.*[47] suggests that the free water that stands on the surface and interstitially between grains is selectively heated by the MWH and ends up vaporizing. However, the remaining water is bound water and does not exert vapor pressure within the system, actually, it keeps absorbing microwaves and heating the system instead. Therefore, for this work, reconstituted gangue samples with higher the fines content are expected to exhibit a higher maximum temperature due to the microwave energy absorbed by the bound water. However, the authors found temperatures above 250 °C, significantly superior to the temperatures recorded in this work. Nonetheless, the purpose of their study was to investigate the bitumen extracting using MWH their samples were raw low-grade ore containing 7 % of bitumen and approximately 4 % water. The samples investigated in this work are NAE reconstituted gangue, containing water, cyclohexane, and only a small fraction of bitumen. In this sense, the capacity of the water to bound with fines present in the NAE reconstituted gangue is different than that in the raw oil sand ore.

Overall, this work considers the higher final heating temperature in samples with more elevated fines as a coupling effect. In other words, at least a small fraction of the water is expected to be bound with the hydrophilic fines promoting a more elevated final heating temperature as suggested by Robinson *et al.*[47]. Also, it is believed that the water vapor further heats before leaving the sample, as proposed by Khalkhali *et al.*[28].

Additionally, average temperature more elevated in samples with higher fines content was also observed by Hussein[78]. Moreover, as discussed in Section 4.4, observing higher temperatures in samples with more fines is more evidence that the higher specific surface area of fine particles improves the MWH of the NAE reconstituted gangue samples studied. Finally, samples with the same fines but higher concentrations of cyclohexane also show a more increased average temperature. This was interpreted as a result of having more water (microwave absorber) per unit of mass in these samples.

4.4.2 Results of Samples dried for 780 seconds

Table 4.5 shows results obtained from the of microwave drying of samples with different concentrations of cylohexane, water, and fines content for 780 seconds. The results were obtained from the gas chromatography analysis of mixture from the toluene-liquid extraction process of NAE reconstituted gangue samples as discussed in the Section 3.4.

As discussed in the Section 2.2.1 water molecules absorb the incident microwaves increasing their vibrational energy, in a process called selective heating. Subsequently, this energy is transferred to the surroundings. Over time, cyclohexane absorbs this energy, vaporizes and diffuses towards the direction of lower pressure, that is, the top of the vial. During this process, as it is a porous media molecules of cyclohexane may get trapped within the pores.

In the second stage, the water turns into vapor and diffuses upwards, as observed in the second plateau in Figure 4.3. Indeed, the water vapor acts transferring energy to potential remaining cyclohexane molecules that might have been trapped in the porous media during the first stage. As a consequence, the steam acts stripping the residual cyclohexane from the sample [46].

As shown in Table 4.5, the results show that a ratio of 1/2 of water to cyclohexane was sufficient to reduce the concentration of cyclohexane in the reconstituted gangue to levels

Table 4.5: Results of microwave drying of reconstituted oil sands ore gangue for 780 seconds

Sample	**Cyclohexane (wt%)**[1]	**Water (wt%)**[2]	**Fines (wt%)**[3]	**Bitumen (wt%)**[3]	**Concentration of cyclohexane after 780s of MW drying** [4]
CH06_W02_10F	6	2	10	1	Not-detected [5]
CH06_W03_10F	6	3			Not-detected
CH12_W04_10F	12	4			(289 ± 71) ppm
CH12_W06_10F	12	6			Not-detected
CH06_W02_20F	6	2	20	1	Not-detected
CH06_W03_20F	6	3			Not-detected
CH12_W04_20F	12	4			Not-detected
CH12_W06_20F	12	6			Not-detected

[1] wt% in wet basis.
[2] wt% in dry basis.
[3] wt% based on soxhlet solids only.
[4] The limit of quantification of the chromatography method is 150 ppm.
[5] An extra amount of 0.5% of cyclohexane was added in this sample.

below the targed of 250 ppm for all samples tested. Nonetheless, in high fines samples, a 1/3 ratio proved enough to remove cyclohexane to values below the threshold. As discussed in Section 4.4, this effect was attributed to the higher energy transfer efficiency observed in samples with higher fines content due to the larger specific surface area of fines compared to coarse particles.

The samples containing 6 wt% cyclohexane and 1/3 ratio of water showed a recovered cyclohexane result below the threshold even having low fines content. It is proposed that the lower the initial concentration of cyclohexane the lower probability of having cyclohexane molecules trapped within the porous. Thus, a 1/3 water-cyclohexane ratio seems to be sufficient to remove cyclohexane from the gangue to levels below the threshold for low initial concentrations of cyclohexane. Indeed, this result indicates steam stripping as one of cyclohexane removal mechanisms.

The results obtained agree with the results of microwave drying obtained by Khalkhali *et al.*[28] for samples with a similar composition. In their work, Khalkhali *et al.*[28] observed a residual concentration of 347 ± 75 ppm for a sample with 4 % water, 12 % cyclohexane (in dry basis) and approximately 7 % fine solids. This work obtained (289 ± 71) ppm of residual cyclohexane in a sample with 4 % water (solvent-free basis), 12 % cyclohexane (wet basis) and 10 % fines. In addition, a sample containing 6 % water , and 12 % cyclohexane (wet basis) revealed residual cyclohexane below the limit of quantification of 150 ppm. In their work, Khalkhali *et al.*[28] did not detect residual cyclohexane for the corresponding sample.

4.5 Drying Rate

According to the results discussed in the previous Section, drying rate curves were obtained using a water-cyclohexane ratio of 1/2 for the following samples:

- CH12_W06 – 10 % fine solids
- CH06_W03 – 10 % fine solids
- CH12_W06 – 20 % fine solids
- CH06_W03 – 20 % fine solids

The reconstituted gangue samples went through microwave heating for 4 different times. The criteria to obtain these data points were based on the temperature profile observed in Figure 4.3. As discussed in Section 4.4, the microwave drying exhibited three plateaus. Therefore, as suggested by Khalkhali *et al.*[28], the microwave drying process was stopped at the time which the first and the second plateau terminated, at the time the system reached the maximum temperature, and after 780 seconds of microwave heating. Moreover, the concentration of cyclohexane in the reconstituted gangue prior to drying was also measured yielding a total of 5 data points per each set of drying experiment.

4.5.1 Cyclohexane Concentration In The Reconstituted Gangue Samples Prepared

NAE reconstituted gange samples went through liquid-liquid extraction to evaluate the cyclohexane concentration in the samples prior to MWH. Table 4.6 shows the results obtained from gas chromatography analysis of the extracted liquid. These values demonstrate that there is a difference between the concentration of cyclohexane added to the reconstituted gangue and the actual values measured prior to starting the drying. This difference reflected solvent losses during the reconstituted gangue preparation, handling, storage, and packing before being submitted to drying, as also observed by Panda *et al.*[27] and Khalkhali *et al.*[28].

Table 4.6: Results obtained from the liquid extraction by toluene + GC for reconstituted gangue samples tested

Reconstituted Gangue	**Fines Content wt% in DSBS**	**Results Obtained From the Liquid Extraction + GC**
Cyclohexane 12 wt%, Water 6 wt%	10	(10.3 ± 0.7) wt% Cyclohexane
Cyclohexane 12 wt%, Water 6 wt%	20	(11.2 ± 0.8) wt% Cyclohexane
Cyclohexane 6 wt%, Water 3 wt%	10	(4.4 ± 0.3) wt% Cyclohexane
Cyclohexane 6 wt%, Water 3 wt%	20	(5.2 ± 0.3) wt% Cyclohexane

The process to obtain the reconstituted gangue samples shown in Table 4.6 mimicked the sampling preparation to obtain the drying points in the curves shown in Figures 4.8 to 4.11. Therefore, these values of concentration of cyclohexane were used as the reference concentration of cyclohexane in the reconstituted gangue. In other words, the results in Table 4.6 reveal the concentration of cyclohexane at the time zero of microwave heating drying for each set of experiments.

Another point that is worth mentioning about the measurements shown in Table 4.6 is the fact that the higher fines samples exhibit a lower difference from the actual concentration of cyclohexane added. In fact, the air drying process of gangue samples that takes place during the sampling preparation and handling occurs in two stages. Stage one is fast and is governed by the evaporation of cyclohexane and the second is a slow evaporation stage of water [17, 24, 25, 27]. As a result, stage one is accountable for the most significant cyclohexane evaporation [25]. Khalkhali and Choi[25] and Ikenna Ejike[32] did not observe a significant oveall change in the cyclohexane flux in samples with higher fines content. However, Ikenna Ejike[32] reported a reduction in stage one duration in samples with high fines content. In this manner, as the reconstituted gangue preparation in this work followed the same protocol for both low and high fines samples, the time spent in their preparation was also the same. As a result, the solvent loss during the preparation and handling of the samples with high fines content was expected to be lower than in low fines reconstituted gange samples, as indicated in Table 4.6.

All in all, NAE reconstituted gangue samples with a controlled amount of cyclohexane, water, and fines were obtained. NAE reconstituted gangue samples were prepared following a well-established methodology first proposed by Panda *et al.*[27]. Additionally, the concentration of cyclohexane in the NAE reconstituted gangue was obtained following a new method first proposed by Khalkhali *et al.*[28]. In this manner, results confirm that the methodology proposed by Khalkhali *et al.*[28] is repeatable with reasonable uncertainties and accuracy.

4.5.2 Drying Rate Curves

Figures 4.8a presents the results obtained for drying samples of low fines reconstituted gangue containing 12 wt% cyclohexane, 6 wt% water, and 10 wt% fines (CH12_W06_10F) with the corresponding error bars. The Y-axis displays the ratio between the measured concentration of cyclohexane at a particular time (C_t) over the initial concentration of the gangue(C_{to}):

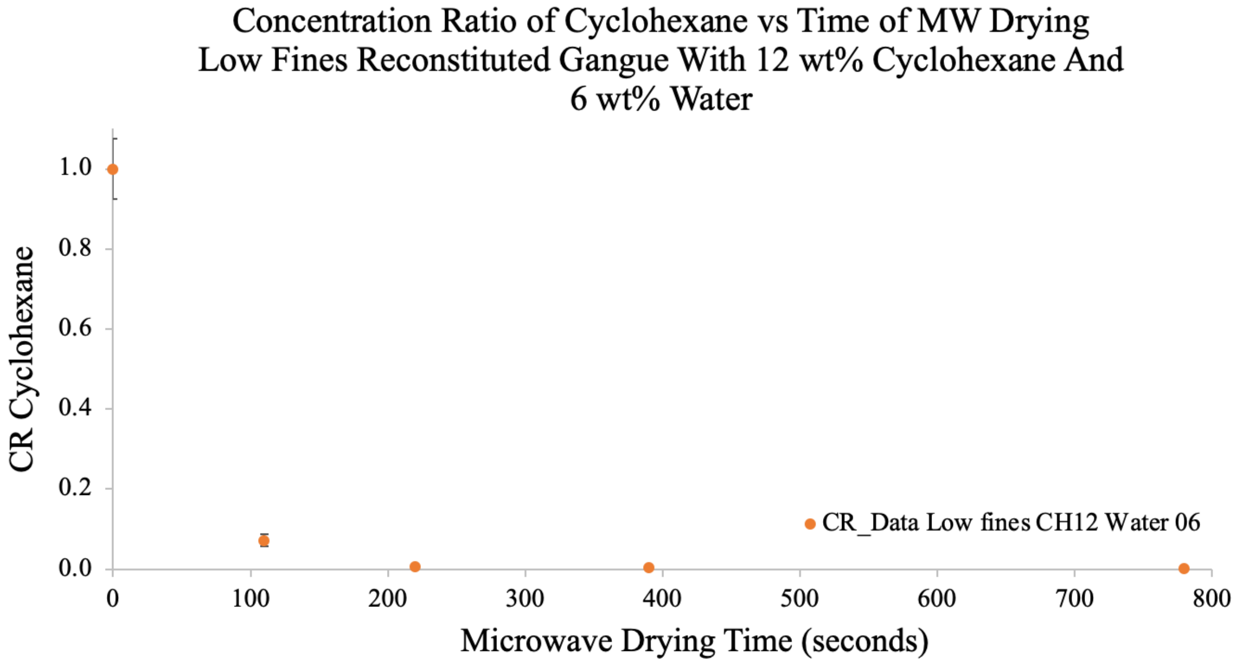
$$CR = \frac{C_t}{C_{to}} \tag{4.1}$$

Figure 4.8b shows a proposed model for the drying process. Overall, a simple Lewis exponential showed revealed an excellent agreement with the experimental data points. Also, the experiments did not yield to points enough to support the development of a more complex model. Therefore, the Lewis model was selected to describe the drying behavior of the reconstituted gangue samples under microwave heating. The Lewis model:

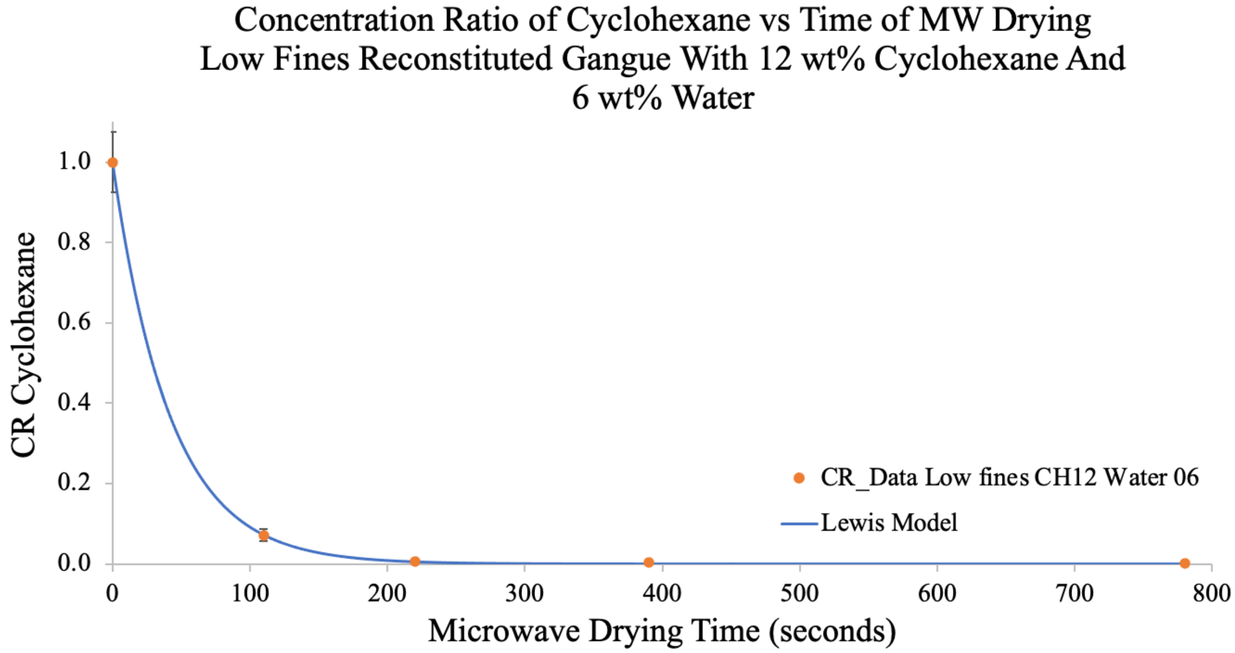
$$C_{CH}(t) = e^{-kt} \tag{4.2}$$

Where, C_{CH} is the concentration of cyclohexane in the reconstited gangue over the time, k is the drying constant (s^{-1}) and t the time (s).

Figure 4.9 shows the experimental results of microwave drying and the Lewis model for



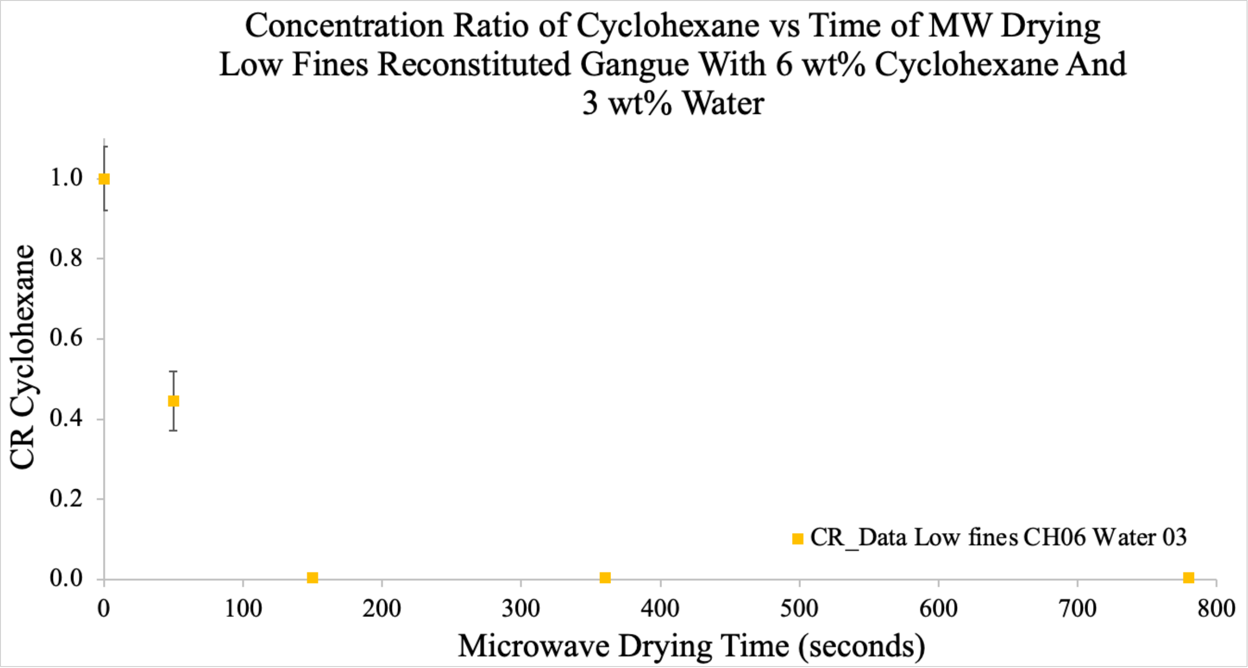
(a) Microwave drying of low fines reconstituted gangue samples with 12 wt% cyclohexane and 6 wt% water.



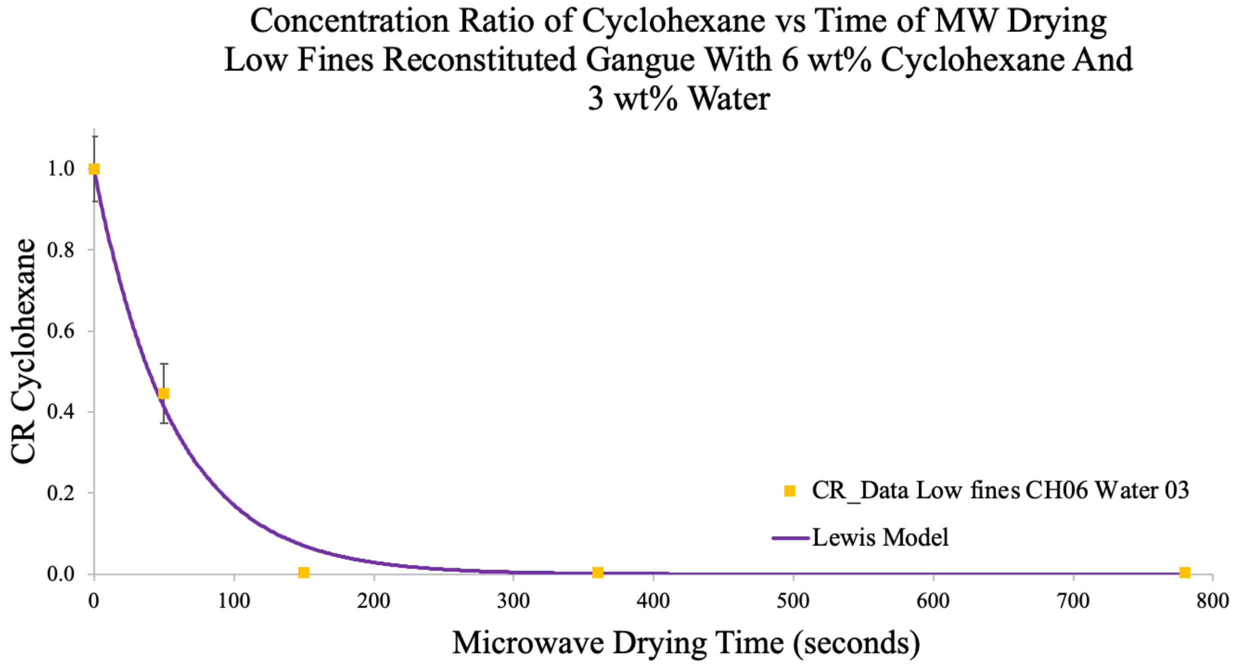
(b) Lewis model applied to experimental data of microwave drying of low fines reconstituted gangue samples with 12 wt% cyclohexane and 6 wt% water.

Figure 4.8: Experimental data and Lewis model for microwave drying of low fines reconstituted gangue samples with 12 wt% cyclohexane and 6 wt% water.

low fines samples containing 6 wt% cyclohexane, 3 wt% water. Likewise, the results for samples containing high fines are shown in Figures 4.10 and 4.11.

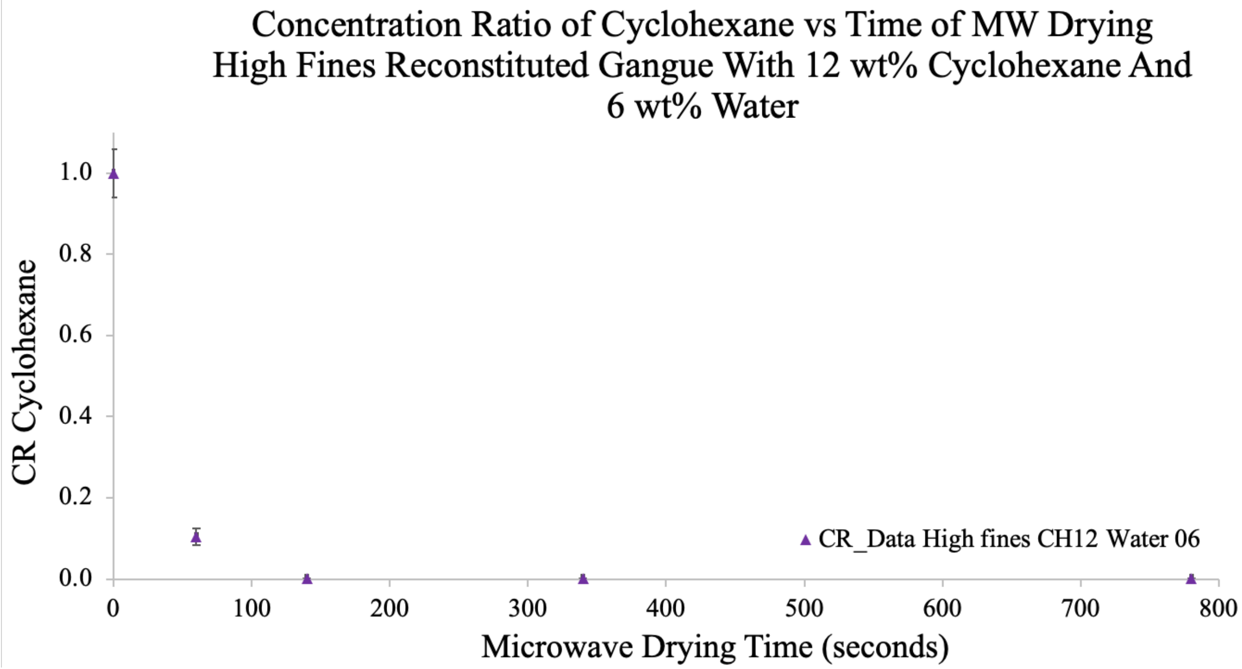


(a) Microwave drying of low fines reconstituted gangue samples with 6 wt% cyclohexane and 3 wt% water.

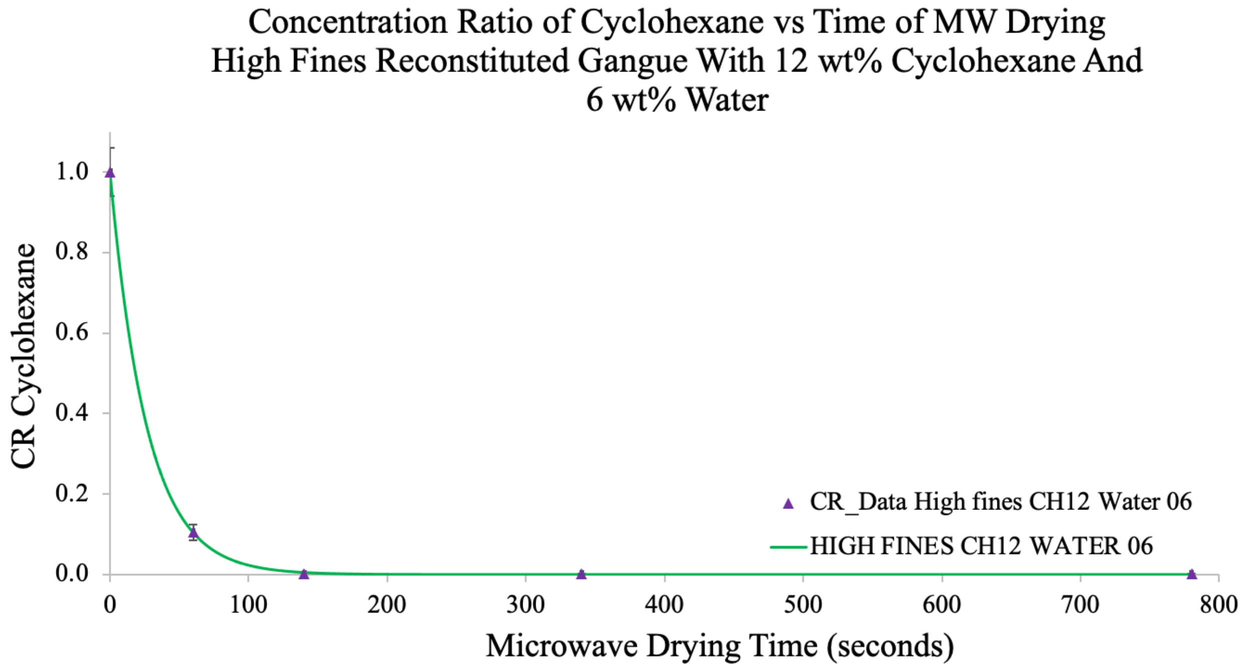


(b) Lewis model applied to experimental data of microwave drying of low fines reconstituted gangue samples with 6 wt% cyclohexane and 3 wt% water.

Figure 4.9: Experimental data and Lewis model for microwave drying of low fines reconstituted gangue samples with 6 wt% cyclohexane and 3 wt% water.

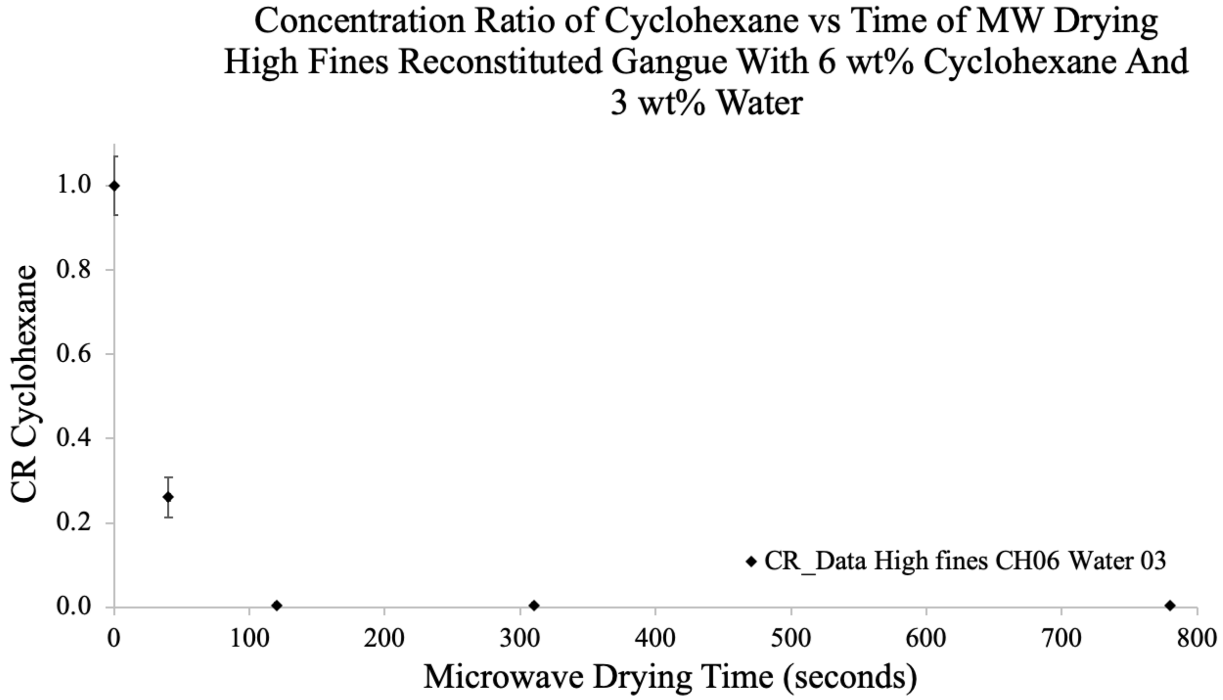


(a) Microwave drying of high fines reconstituted gangue samples with 12 wt% cyclohexane and 6 wt% water.

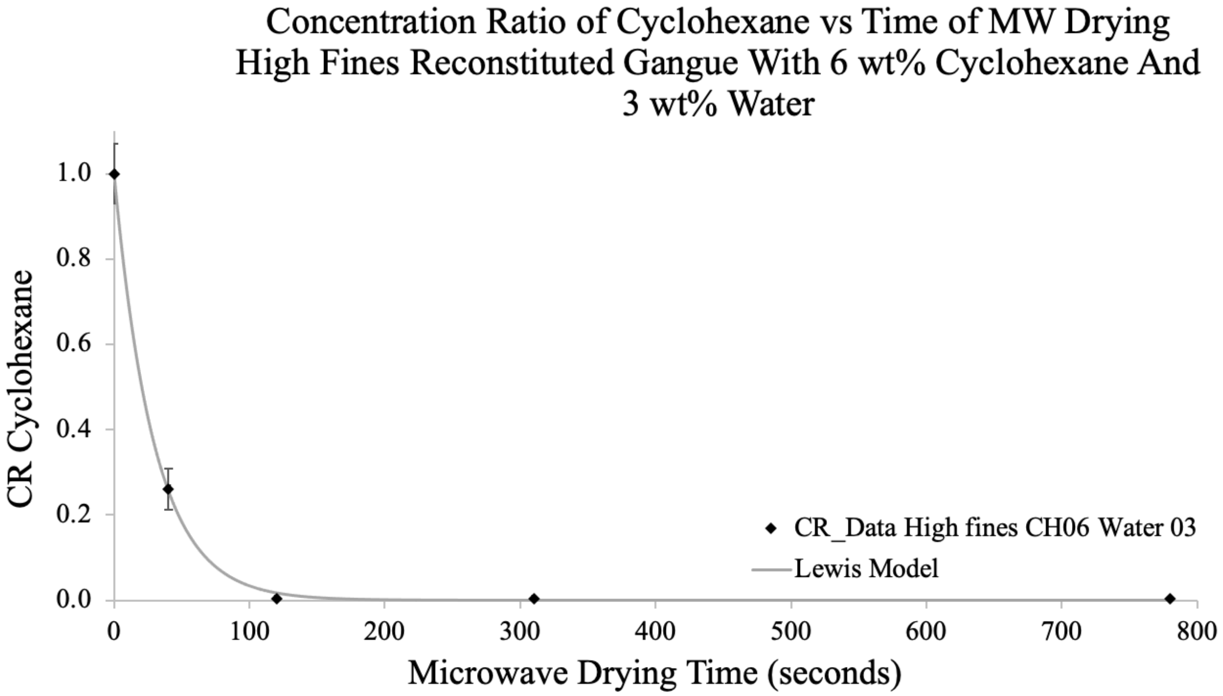


(b) Lewis model applied to experimental data of microwave drying of high fines reconstituted gangue samples with 12 wt% cyclohexane and 6 wt% water.

Figure 4.10: Experimental data and Lewis model for microwave drying of high fines reconstituted gangue samples with 12 wt% cyclohexane and 6 wt% water.



(a) Microwave drying samples of high fines reconstituted gangue sample with 6 wt% cyclohexane and 3 wt% water.



(b) Lewis model applied to experimental data of microwave drying of high fines reconstituted gangue sample with 6 wt% cyclohexane and 3 wt% water.

Figure 4.11: Experimental data and Lewis model for microwave drying samples of high fines reconstituted gangue sample with 6 wt% cyclohexane and 3 wt% water.

The results of the statistical analysis of the Lewis model applied to experimental data of microwave drying of all scenarios tested samples are shown in Table 4.7. Values of R-square (R^2) of 0.99 and small values of Chi-square (χ^2), and root mean squared error (RMSE) indicate that the model can describe with a satisfactory level o accuracy the microwave drying behavior of the reconstituted gangue samples. There was not available in the open literature a work that proposed drying models for microwave drying of oil sands gangue samples. However, semi-theoretical such as Lewis, Page model, and its modified forms commonly show a good performance to describe the behaviors of microwave heating of food material and [79, 80]. In addition, exponential decay showed a great performance for describing contaminant removal from hydrocarbon-contaminated soil samples using MWH [46, 81, 82].

The model was validated using the microwave heating data published by Khalkhali *et al.*[28]. Figure 4.12 shows the Lewis model applied to their data, and Table 4.8 shows the statistics analysis of the data. The concentrations of cyclohexane in wet basis reported by the authors was 10.3 wt%. The amount of water in the water (solvent-free basis) was 5.6 % and the fines content was 6.8 %.

Table 4.7: Results of statistical analysis of Lewis model applied to microwave drying of NAE resconstited gangue samples

Sample	**Estimated Parameter K** (s^{-1})	R^2	**RMSE**	χ^2
CH12_W06_10F	0.0239	0.99	1.80E-03	3.38E-06
CH06_W03_10F	0.0177	0.99	3.73E-02	1.39E-03
CH12_W06_20F	0.0377	0.99	2.10E-03	4.52E-06
CH06_W03_20F	0.0339	0.99	7.60E-03	5.71E-05

Table 4.8: Results of statistical analysis of Lewis model applied to Khalkhali *et al.*'s[28] results

Sample	**Estimated Parameter K** (s^{-1})	R^2	**RMSE**	χ^2
Khalkhali *et al.*'s[28] results	0.0281	0.99	6.10E-03	3.71E-05

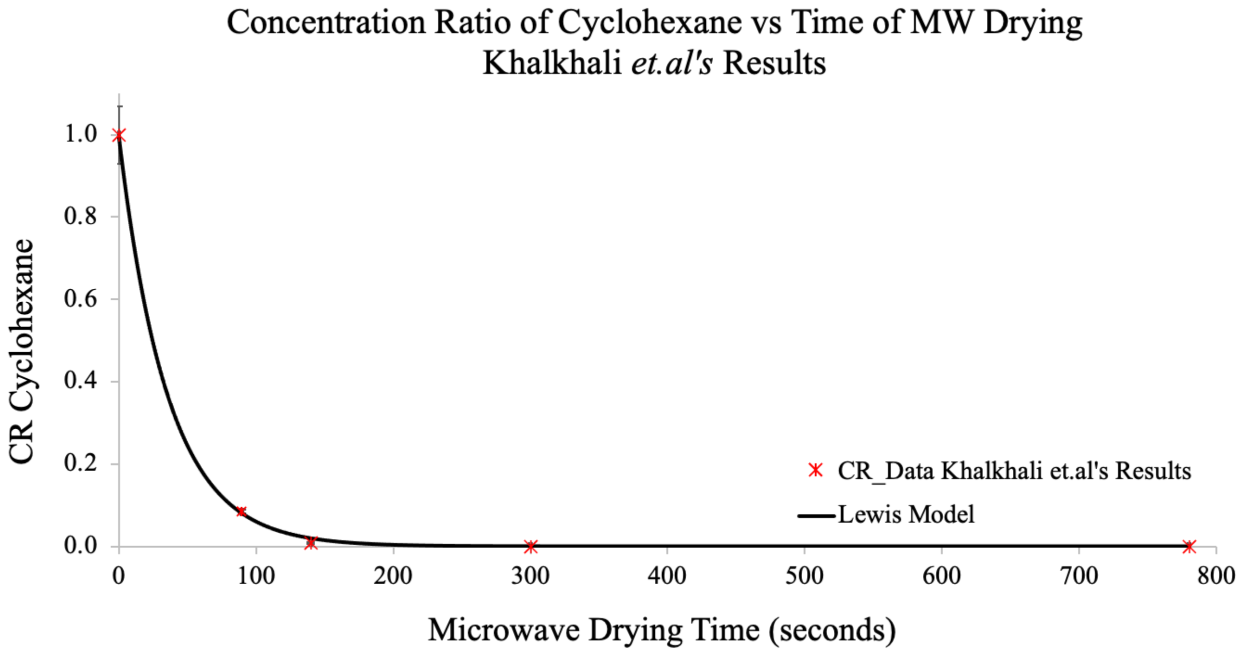


Figure 4.12: Lewis proposed model applied to Khalkhali *et al.*'s[28] microwave heating data of results.

Therefore, the results obtained from this work exhibited a satisfactory correspondence with the previous literature available. The removal of cyclohexane of non-aqueous gangue by microwave follows an exponential behavior with a rapid decaying. Within a few minutes, the concentration of cyclohexane drops from 6 or 12 wt% to a few hundred ppm, a drying time significantly shorter than the air drying [27, 28]. Moreover, compared to conventional heating, vacuum conditions of 30 kPa or higher combined with temperatures around 80 – 100 °C were required to reduce the concentration of cyclohexane to the target value of 250 ppm in the order of time as MWH [26].

4.5.3 Optimum Microwave Heating Drying Time.

Following the methodology proposed by Khalkhali *et al.*[28] the samples were exposed to microwave heating for a total time of 780 seconds. A ratio of cyclohexane to the water (MW absorber) was considered satisfactory if the residual concentration of cyclohexane after 780 seconds reached values equal to or below 250 ppm. Nevertheless, results indicate that as long as the proper cyclohexane-water ratio was used in the reconstituted gangue samples the concentration of cyclohexane achieved the concentration threshold in shorter times. Due to the limitations of experimental data points, it was not possible to determine the precise time when the 250 ppm was achieved for all the samples, however, the results indicate that 250 to 300 seconds would be enough to reduce the cyclohexane concentration to values needed. In fact, these findings agree with the previous literature [28] and reinforce the capability of microwave heating to provide rapid, selective, and efficient heating of reconstituted gangue samples.

4.5.4 Effect of Fine Particles On The Drying Rate of Reconstituted Gangue.

As discussed in the previous Section, NAE reconstituted gangue samples containing low and high fines content were dried using microwave heating. Figure 4.13 shows the effect of increasing fines in reconstituted gangue samples. Figure 4.13a displays the results for the gangue samples containing 12 wt% cyclohexane and 6 % water, and Figure 4.13b 6 wt% cyclohexane and 3% water. According to the Figures and the values of the parameter K shown in table 4.7, the samples containing more fines have a more accentuated exponential decay than the samples with lower fines content.

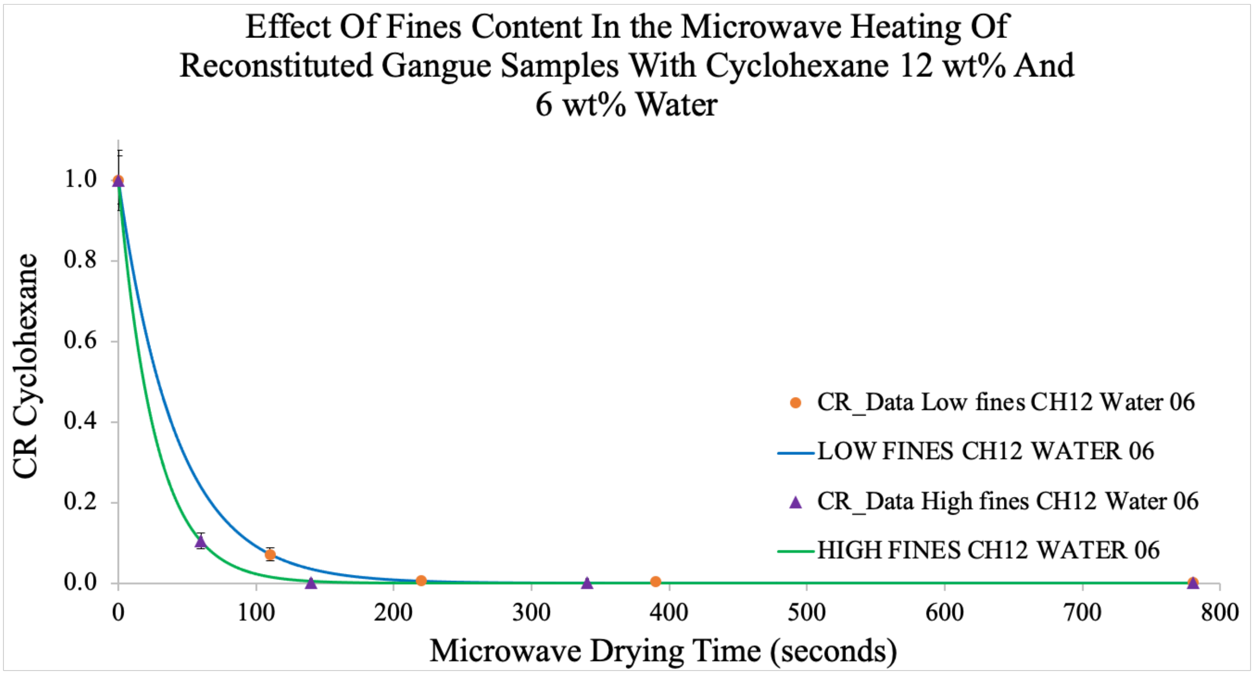
This result was surprising considering the results from the previous open literature. Renaud *et al.*[26] investigated removing cyclohexane of NAE gangue under conventional heating and vacuum. They noticed that low-grade samples (higher in fines and water content) required a time to achieve a residual concentration of 250 mg/kg more than 3 times compared to gangue from high-grade (lower in fines and water fraction). The authors referred to this behavior as a potential clogging of the material porous caused by the high fines and water content. Regarding works that applied air drying to remove cyclohexane from NAE reconstituted gangue samples, Ikenna Ejike[32] observed an increase in residual cyclohexane when fines increased; however, after two hours of drying the final concentration of cyclohexane was below the threshold of 250 ppm. Additionally, Khalkhali and Choi[25] observed that increasing fines content lowered the mean pore size in the samples which would decrease the evaporation of cyclohexane. Nonetheless, they discussed that samples with higher fines show higher hydrophobicity – due to the precipitation of asphaltenes in fine solids [74]– which should favor the formation of cyclohexane liquid film boosting the evaporation. Eventually, the authors argue that these two factors canceled with each other yielding no noticeable influence on the cyclohexane drying rate when fines samples were increased.

Falciglia *et al.*[83] studied the thermal desorption of coarse, medium, and fine sand, silt, and clay samples contaminated by diesel using a tubular electric furnace. They observed that higher temperatures were needed to remedy silt and clay samples due to a higher affinity of these soils to adsorb alkanes, however, these smaller particles exibited a higher heating rate.

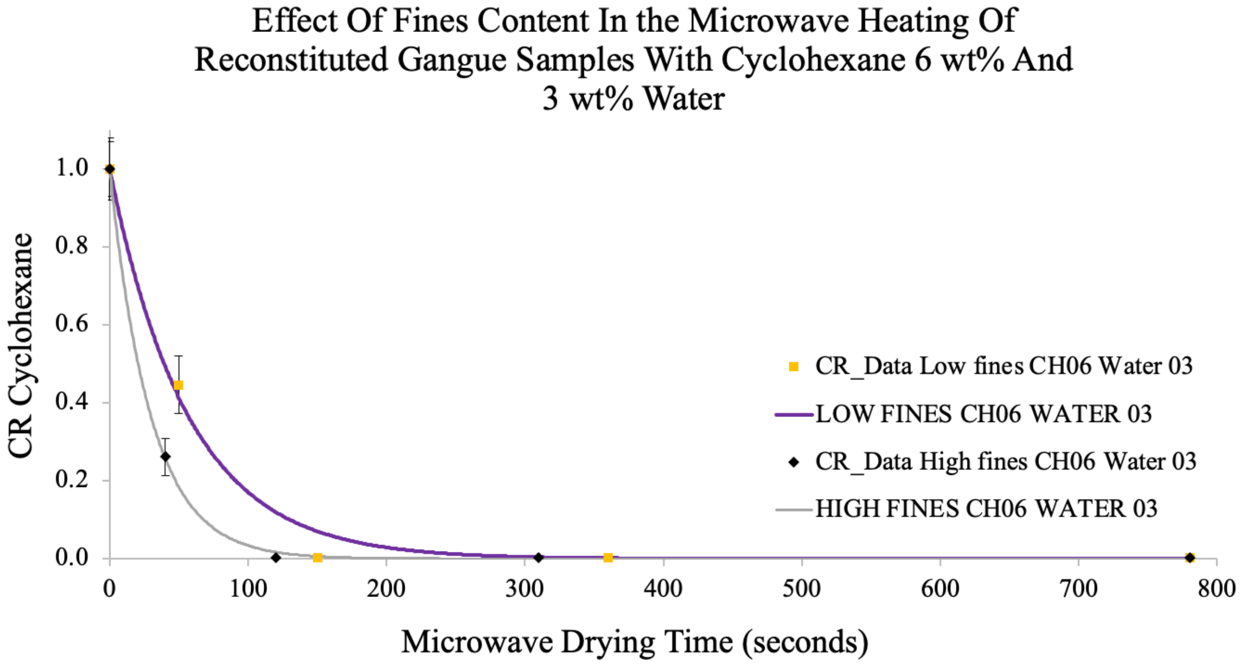
Qi *et al.*[84] investigated the effect of particle size on the thermal desorption of soil contaminated with semivolatile polychlorinated biphenyls (PCBs) applying conventional heating. The authors noticed a better removal efficiency of PCBs in soil with smaller particles. They attributed this difference to factors such as changes in specific surface area, internal pore size, and physical-chemical properties.

In this work, the faster decaying of samples with higher fines content was attributed to the fact that fine particles exhibit specific surface area significantly larger than coarse particles. Therefore, the microwave selective heating process is expected to be more efficient in these samples. Consequently, heat transfer between the water (microwave absorber) and the surroudings is enhanced, thus the removal rate of cyclohexane is favoured. Such results demonstrate an improvement compared to conventional heating which is about 3 times slower for low-grade ore (higher fines content).

Additionally, as discussed in the Introduction, Section 1, the tailing management of the current water-based process is quite challenging, particularly due to the presence of fine particles in the oil sand ore. In this sense, these findings indicate that applying microwave heating to recovering cyclohexane from NAE gangue would broaden the performance of the non-aqueous process as it exhibits an even better performance in the presence of high fine solids.



(a) Effect of fines content in the microwave heating of reconstituted gangue samples containing 12 wt% cyclohexane and 6 wt% water



(b) Effect of fines content in the microwave heating of reconstituted gangue samples containing 6 wt% cyclohexane and 3 wt% water

Figure 4.13: Effect of fines content in the microwave heating of reconstituted gangue samples.

4.5.5 Effect of Varying The Initial Cyclohexane Concentration On The Drying Rate of Reconstituted Gangue.

Figure 4.14 compares the drying curves of low fines reconstituted gangue samples containing 12 and 6 wt%, likewise Figure 4.15 contrasts the high fines samples. There is only a small difference between the drying behavior of 12 and 6 wt% cyclohexane for both low and high fines content samples. However, the difference follows the same trend, the higher the cyclohexane composition the faster the exponential decay. In fact, the samples with higher concentrations of cyclohexane also have a more elevated fraction of water (microwave absorber), which could justify this small difference in the drying rate.

Nonetheless, considering the measurement uncertainties the difference in the drying rate of 12 and 6 wt% cyclohexane fades out for both low and fine content samples. In that manner, it is concluded that altering the initial reconstituted gangue concentration does not play an important role in the drying rate of the process as varying the fines content does.

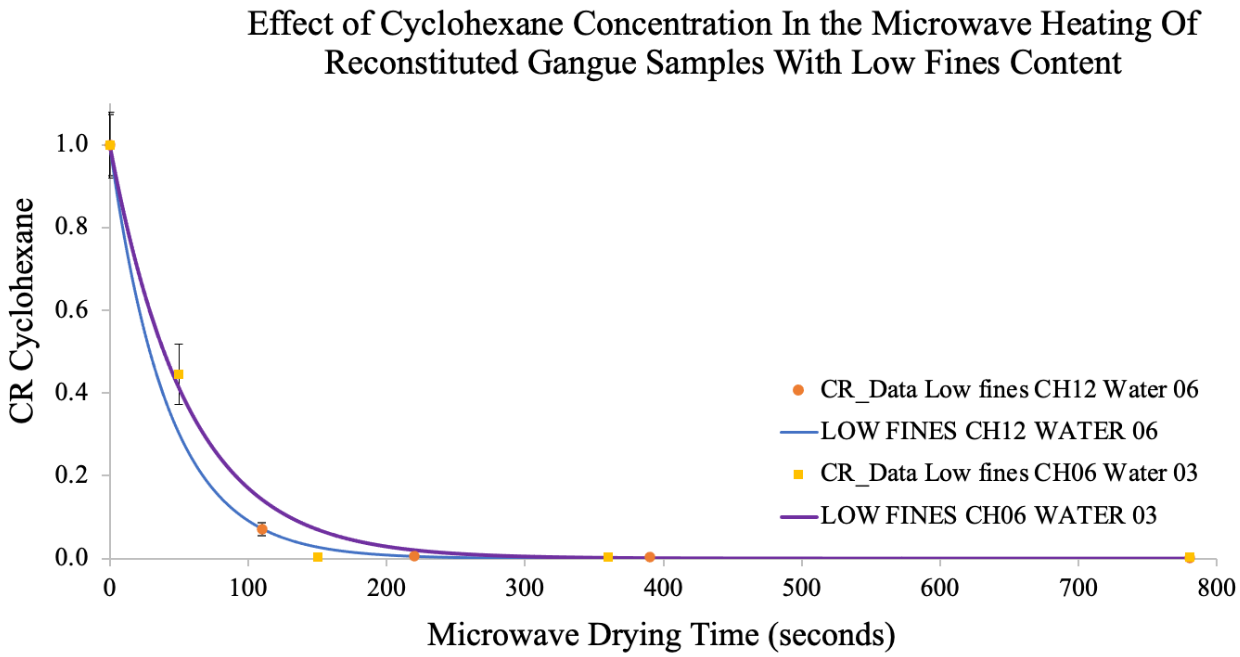


Figure 4.14: Effect of varying the initial concentration of cyclohexane in the drying rate of low fines reconstituted gangue samples

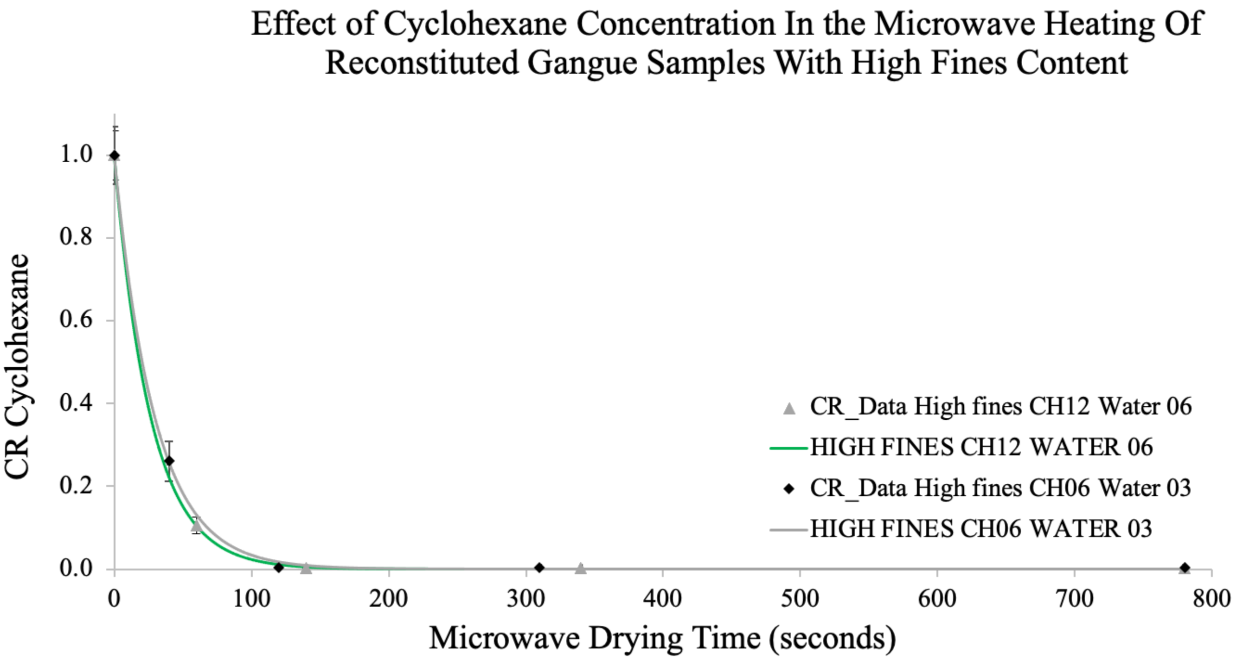


Figure 4.15: Effect of varying the initial concentration of cyclohexane in the drying rate of high fines reconstituted gangue samples.

4.5.6 Limitations Of The Model and The Experimental Apparatus

As discussed in Section 4.5 to build the drying curves the microwave heating drying was stopped at 4 strategic points, at the time that the system achieved the end of the plateaus, the maximum temperature, and after 780 seconds. We tried to collect more points to build the curve by stopping the drying process in between these points, that is, within the plateaus and/or when the temperature was ramping up. However, the results for the residual cyclohexane after the gas chromatography showed uncertainties as high as 70 %, an impractical accuracy.

The system's temperature quickly achieves the boiling point of the cyclohexane in the microwave cavity. Moreover, when the drying is stopped, the sample has to be rapidly removed from the microwave heating cavity, capped, sealed with Parafilm, and cooled down as quickly as possible. Therefore, if the system is not stable enough the readings become inoperable.

In this manner, to further investigate the effect of microwaves on recovery cyclohexane from NAE reconstituted gangue a microwave setup in which the cavity is connected to gas chromatography equipment is advised. This setup would provide online measurements of residual cyclohexane over time with practical levels of accuracy for several data points.

5. Conclusion and Future Work

In this work microwave heating of non-aqueous extraction oil sand ore gangue was performed. A reconstituted gangue protocol to obtain samples with controlled concentrations of cyclohexane, water, bitumen, and fines was successfully implemented. Hence, the natural variability expected for a typical gangue sample was circumvented.

Due to the microwave absorbing capability of water, we first investigated the optimal water/cyclohexane mass ratio able to remove cyclohexane from the gangue to levels below a threshold of 250 ppm. In this sense, reconstituted gangue samples with a fixed amount of bitumen (1.08 ± 0.08) wt%, 10 and 20 % fines, 6 and 12 wt% of cyclohexane and mass ratios of water/cyclohexane of 1/3 and 1/2 underwent 780 seconds of MWH.

The temperature profile obtained during the MWH showed three plateaus of temperature. The first one happening approximately 68 °C, indicating the evaporation of cyclohexane, and the second $\sim$ 100 °C signifying the evaporation of water. Moreover, a maximum temperature plateau recorded during the MWH experiments, which was higher for samples with more fines content. This behaviour was attributed to a coupling effect of overheating water bound within the fine particles and the further heating of water vapour prior to leaving the samples.

The microwave dried samples went through a liquid-liquid extraction process using toluene to extract the residual cyclohexane in the gangue after the microwave drying process. A gas chromatography method with an internal standard was successfully developed and applied to quantify the cyclohexane in this liquid mixture. Thus, the residual concentration of cyclohexane in the microwave-dried gangue samples was obtained.

The results reveal that a 1/2 water/cyclohexane mass ratio in the reconstituted gangue was sufficient to reduce cyclohexane concentration to values below the threshold regardless the concentration of fines and/or cyclohexane. Nonetheless, for high fines content reconstituted gangue samples, a 1/3 mass ratio showed to be enough. This was attributed to the higher energy transfer efficiency observed in samples with higher fines content due to the larger specific surface area of fines compared to coarse particles. In addition, samples with initial 6 wt% of cyclohexane also required a 1/3 water-cyclohexane mass ratio, regardless the fines content. It was proposed that samples with lower initial concentration of cyclohexane should have a lower probability of having cyclohexane molecules trapped within the porous matrix. Consequently, it was revealed that a 1/3 ratio would be sufficient to perform the drying process.

As the 1/2 water-cyclohexane mass ratio was able to remove the solvent to values below 250 ppm from all the samples tested, the microwave drying curves were obtained using this ratio. Each curve was based on the results of residual cyclohexane observed over five different microwave heating times. A simple Lewis exponential described the experimental microwave drying data satisfactory level of accuracy. Values of R^2 of 0.99 and small values of χ^2 and RMSE were obtained for the statistical analysis of the model applied to all drying curves investigated.

The results obtained desmonstrate that higher fines content resulted in a shorter vaporization time, a higher maximum temperature, and a faster solvent removal rate, regardless of the initial cyclohexane concentration. As discussed previously, these results were attributed to an increase in the specific surface area of fine particles. These findings reveal an improvement compared to both air drying and conventional heating techniques. Under MWH cyclohexane can be removed from NAE gangue within a few minutes. Results from the previous literature indicate that air drying requires two hours to obtain low levels of residual cyclohexane. Additionally, compared to conventional heating vacuum of 30 kPa or higher combined with temperatures $\sim 80-100$ °C would be required to perform the cyclohexane removal at a times similar to the times obtained for MWH. Besides, conventional heating performance is approximately three times slower for low-grade ore (higher in fine solids).

Based on the previous literature, two mechanisms were proposed for the MWH removal of cyclohexane from NAE reconstituted gangue, selective heating and water vapour stripping. In the fisrt, water is selectively heated by microwaves and transfer the energy to the cyclohexane which vaporizes. In the second, cyclohexane is stripped from the sample by the water steam generated in the MWH process.

Overall, the findings demonstrate that microwave heating technology can effectively recover cyclohexane from non-aqueous gangue across different concentrations of cyclohexane, water, and fine solids. This process demonstrates superior efficiency compared to previously explored methods such as air drying and conventional heating and requires only a minimal water-cyclohexane mass ratio to drastically reduce cyclohexane in the gangue within a few minutes. Additionally, results indicate that an increase in fine particle content improves the solvent recovery process. This represents a significant advantage over water-based processes, which are notably sensitive to the presence of fines. These findings obtained were relevant and important to support the further development of an efficient and economically viable microwave facility to recover cyclohexane from NAE oil sand gangue. In this manner, contribute to establishing the groundwork for the development of a more environmentally sustainable NAE technology and align with the objectives of the oil sands industry in achieving net zero emissions.

5.1 Future Work

In this work, the reactor diameter and sample bed height were 19 mm and 15 mm, respectively. At this scale, the effects of the microwave penetration depth, D_p, would not be traceable. Nevertheless, previous studies indicate that the penetration depth for soils is in the order of centimeters. Falciglia and Vagliasindi[82] studied the use of MWH to remove of diesel from different soil samples and concluded that a soil layer for large-scale projects should not exceed 70 cm. In this sense, considering that the bitumen extraction from the open-pit mined oil sand ore operates on a large scale, a penetration depth study of the NAE gangue before scaling up the process is strategic.

Therefore, one could investigate the penetration depth for the NAE reconstituted gangue for industrial-relevant concentrations for a larger-scale experiment setup. In this manner, one can study the penetration depth of gangue samples over a range of power applied, temperature, and frequency to obtain the optimum operating conditions.

Additionally, as discussed in the text, obtaining the cyclohexane concentration within the plateaus and during the temperature ramping proved to be challenging to the setup used. In this context, one could build a gas-chromatography setup attached to the microwave cavity to collect more data points along the microwave drying experiment. Therefore, additional data points could be collected throughout the microwave drying experiment, facilitating the development of a more robust drying model.

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