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Heavy Oil Production Technology Challenges and the Effect of Nano Sized Metals on the Viscosity of Heavy Oil

A literature review and an experimental study

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Abstract

Heavy oil and bitumen make up 70% of the discovered petroleum resources in the world. Only a very small fraction of these resources have so far been produced, as the recovery techniques available for heavy crudes and oil sands have traditionally been far more expensive than those of conventional oil. However, discovery of easy oil is becoming rarer and rarer, and with oil prices stabilizing at over $100/bbl, oil companies are turning to unconventional resources to satisfy the needs of the market. This sets the ground for heavy oil to make up a larger part of the energy mix in the near future.

This thesis examines the main technological challenges of producing and transporting heavy oil. Much work has been done to improve the efficiency of the upstream and downstream sector, while the midstream has not yet been subject to the same focus. However, this is often a very significant part of the expenses in a heavy oil field development. If the greatest challenges can be addressed and handled properly, there is a significant potential for new projects to become economically feasible.

This thesis also covers a set of lab experiments performed, where nano-sized metal particles are mixed into a heavy crude oil. Nano-particles have seen an increased industry focus over the last decade, with several research projects utilizing them to improve oil recovery factor. In China, several studies have utilized nano-sized metals to catalyze an in-situ upgrading of the heavy oil, in order to decrease viscosity and improve recovery factors. This thesis studies the application of these catalysts in topside facilities at the wellsite, as a significant reduction of viscosity will reduce the need for pumps and flow assurance installations. It is also studied how heating the oil by microwaves may affect viscosity, and how nano-sized metals may impact this process.

Sammendrag

Tungolje og bitumen utgjør i dag 70% av verdens samlede oppdagede petroleumsressurser. Kun en brøkdel av disse har i dag blitt produsert, ettersom utvinningsteknikken for tungolje og oljesand tradisjonelt har hatt langt større kostnader og lavere virkningsgrad enn hva gjelder for konvensjonell olje. Men det går i dag stadig lenger mellom storfunn av såkalt lett olje, og med en oljepris som har stabilisert seg på $100 pr. fat, har oljeselskapene fattet økt interesse for ukonvensjonelle ressurser. Dette bereder grunnen for at tungolje i større grad vil bidra til å dekke verdens energibehov i de kommende årene.

Denne avhandlingen utforsker hovedutfordringene knyttet til produksjon og transport av tungolje. Mye har blitt gjort for å forbedre utvinningsgrad i reservoaret og raffineringsprosessene rundt tungolje, men midtstrømsseksjonen har ikke vært under det samme fokuset. Likevel er dette ofte en stor utgiftspost under utbygging av et tungoljefelt, og transportutfordringer kan hindre utbygging av marginale og avsidesliggende ressurser. Det ligger et stort potensiale i utviklingen av slike ressurser dersom de viktigste utfordringene kan håndteres på en god måte.

Denne avhandlingen dekker også en rekke labforsøk hvor metallpartikler i nano-størrelse ble blandet inn i rå tungolje. Nanopartikler har fått et stadig større fokus i oljebransjen de siste ti årene, med særlig fokus på hvordan de kan forbedre utvinningsgraden i reservoaret. Flere prosjekter i Kina har benyttet nanopartikler som en katalysator for in-situ oppgradering av tungolje, med hensikt å redusere viskositeten og dermed øke utvinningsgraden. Denne avhandlingen ser på hvordan disse katalyserende metallene i fasiliteter plassert nedstrøms for brønnhodet, ettersom en reduksjon av viskositet her vil lette videre transport av tungoljen. Det blir også studert hvorvidt oppvarming med mikrobølger vil påvirke viskositeten, og hvilken effekt nano-metallene vil ha i en slik prosess.

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The work in this thesis was made independently and in accordance with the rules set down by the Examination Regulations made by the Norwegian University of Science and Technology.

Fabian Bjørnseth

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1 On Heavy Oil

Heavy oil represents a large portion of the worlds unproduced discovered hydrocarbon resources. High density and viscosity at atmospheric conditions has traditionally made their recovery very energy demanding compared to lighter crudes, and has resulted in very low recovery factors. For this reason, heavy crudes are an abundant untapped potential energy source, which is expected to be a large contributor to the world's energy needs in the future. However, the technological costs per barrel are currently much higher than for conventional resources.

1.1 Fluid properties

Heavy oil is characterized by low API gravity and high viscosity values. The definitions vary between authors, but the US Department of Energy defines heavy oils to have API gravity between 10^{o} and 20^{o}. Oils heavier than 10^{o} are defined as extra-heavy oils, or natural bitumen if the oil is immobile at reservoir conditions. Figure 1.1 shows a graphic representation of these definitions.

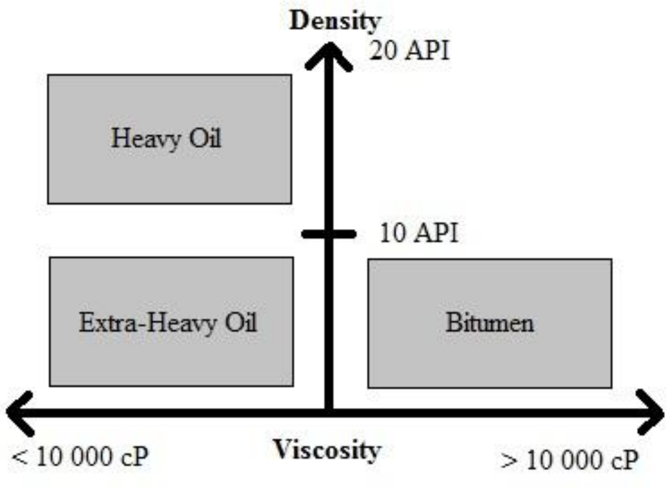

Figure 1.1 – Heavy Oil Classification

The viscosity of heavy crudes is strongly affected by temperature variations. For this reason, thermal recovery methods are commonly used in heavy oil production. Figure 1.2 shows the relationship between viscosity and temperature for two Athabasca bitumen samples.

No universal relationship between oil density and viscosity has been, though generally oils are found to be more viscous when density increases. This is largely due to the presence of asphaltenes, which are large hydrocarbons with high molecular weight that tend to aggregate. Oil viscosity has been shown increase exponentially with asphaltene content. (Ovalles et al, 2011)[2]

Density and viscosity are key properties in determining the economics of a heavy oil field development. Heavy oil generally sells at a lesser price than lighter hydrocarbons, as it will have to go through an energy intensive upgrading process before use. On the other hand, high viscosity values lead to lower production and more expensive EOR investments.

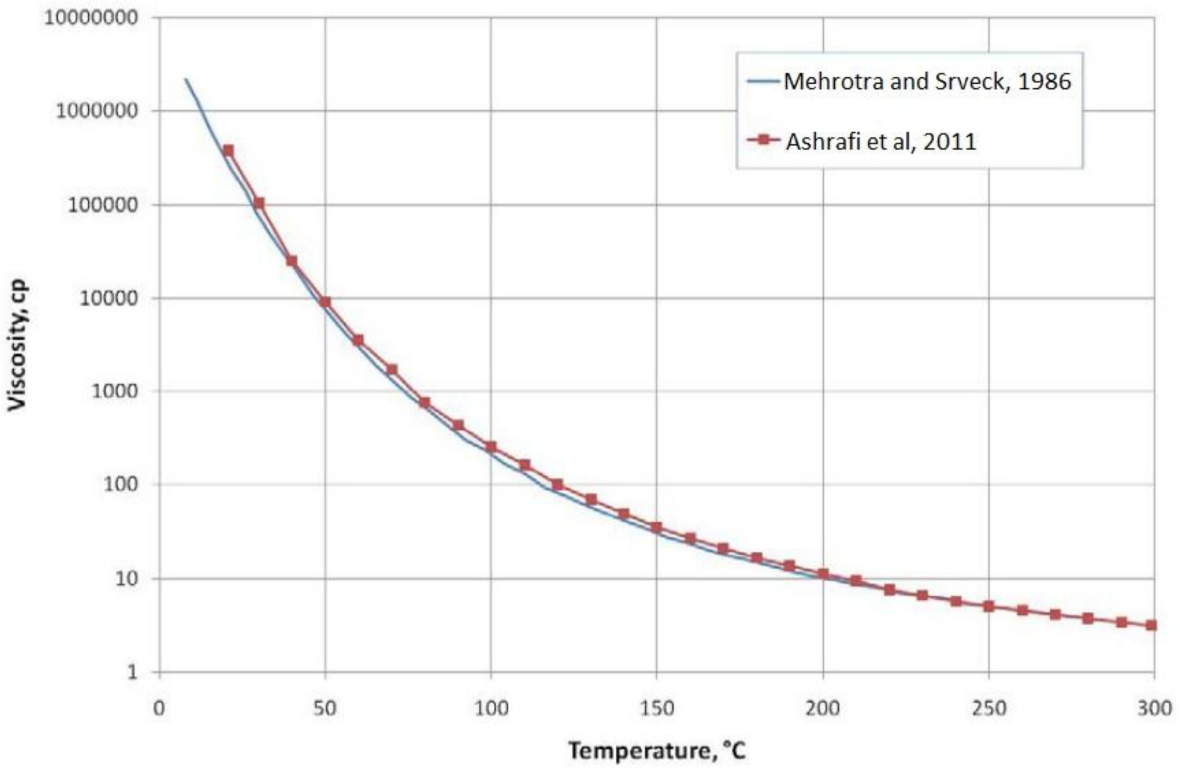

Figure 1.2 – Viscosity – Temperature Relationship of an Athabasca Bitumen

Ashrafi et. al (2011)[1]

1.2 World Reserves

Due to the varying practices in reserve and resource reporting, efforts to chart the world's petroleum reserves by fluid properties are inherently challenging. Paradigm shifts in classification can cause rapid changes in reserve estimates, such as when Venezuela reclassified its' Orinoco heavy oil to proved reserves, bumping the nations' total reserves from 99,4 to 211 billion barrels.

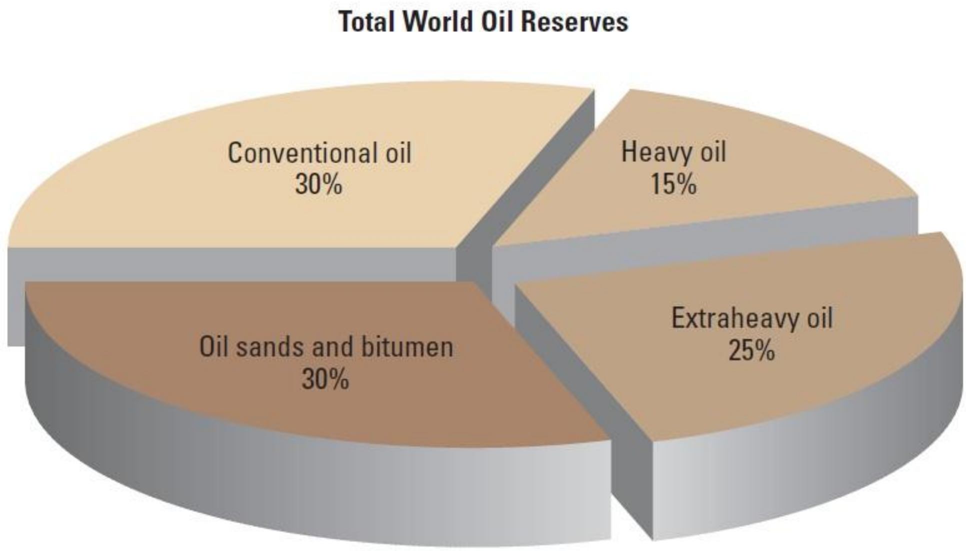

Figure 1.2 – Distribution of Total World Oil Reserves by Classification

Oilfield Review, (2006)[5]

Figure 1.2 shows a frequently cited chart published in Oilfield Review, 2006[5]. Out of the world's total remaining oil reserves, heavy, extra heavy oils and bitumen are expected to make up 70%. This number underlines the increasing importance of heavy oil production going forward, as conventional supplies are decreasing. Data presented by Saniere et al (2004)[4] underline this message. As figure 1.3 shows, heavy oil reserves are approximately the same amount as conventional reserves, but very little of the heavy oil has so far been produced compared to conventional resources. These numbers underline the potential gains from developing more effective extraction and production technology for heavy oil.

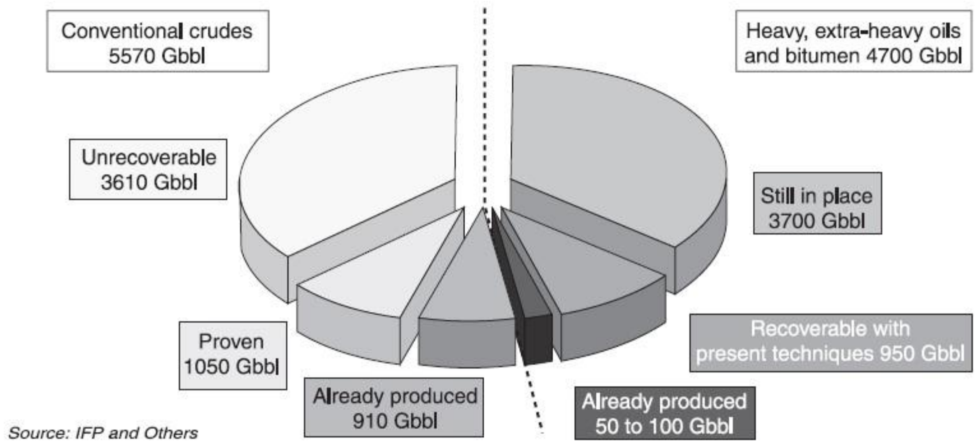

Figure 1.3 – Total World Oil Resources Produced and In Place

Saniere et.al, (2004)

1.3 Locations

Heavy oil is typically found in supergiant, shallow deposits. As a result of this, a few nations hold most of the world's resources and production of heavy oil and bitumen. Saniere et al (2004)[4] reported that 87% of the heavy oil is located in Western Canada, Venezuela and Former Soviet Union states in Eastern Europe. Although the resource estimates are dated, the resource distribution reflects current estimates.

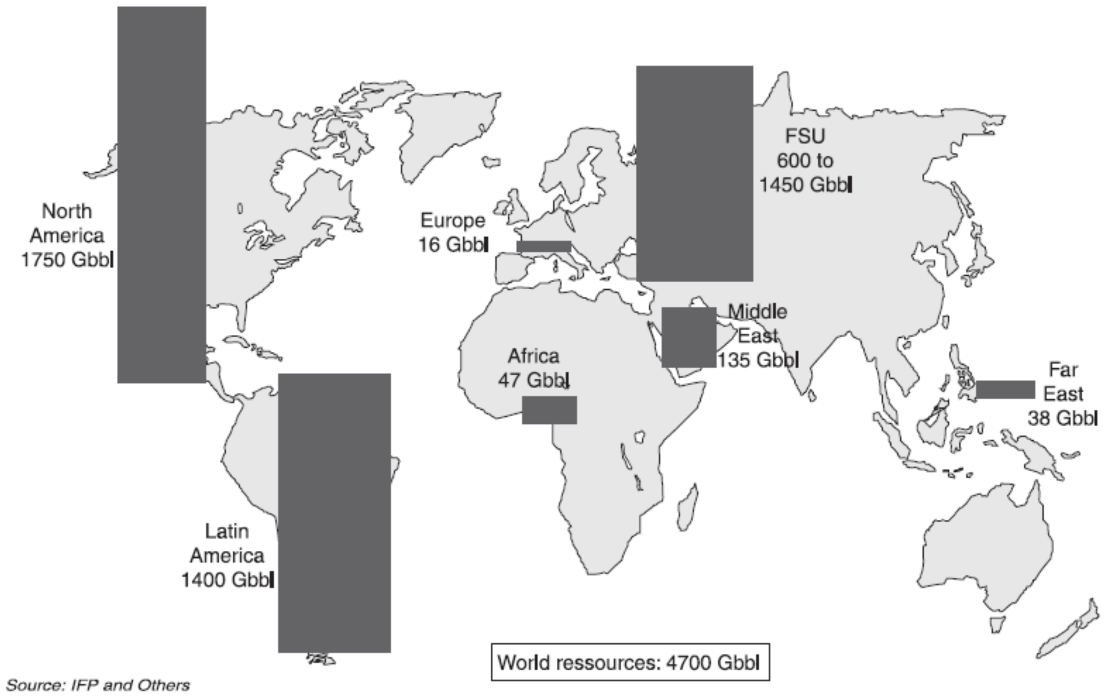

Figure 1.4 – World Heavy Oil Distribution by Location

(Saniere et. al., 2004)

Interestingly, very little of the world's heavy oil resources are found in the Middle East. This sets the stage for geopolitical motivations in the development of heavy oil technology. If significant advancements were made in heavy oil production technology, it might lessen the OECD countries' dependence on imported oil from this region. This may be seen in the same light as how new fraccing technology for shale formations is turning the U.S. into a net exporter of oil and gas.

The Grane Oil Field is the first heavy oil field producing on the Norwegian Continental Shelf. It is operated by Statoil and has been producing since September 2003. It is one of the largest discoveries on the Norwegian continental shelf, and is expected to produce more than 750 million barrels. The produced oil has a 12 cP viscosity and 19^{o} API rating, which makes it heavy by Norwegian standards, but fairly light compared to heavy oil deposits in other countries. This makes it possible to use gas injection to boost oil recovery. 60% of the original oil in place is expected to be recovered by the end of field life, a large value even for conventional oil fields. The produced oil is exported to an onshore terminal through a 28”, 212 km pipeline.

So far, Grane remains the only heavy oil field producing on the NCS. There is, however, heavy oil activity in the British sector of the North Sea, with Statoil set to develop the Mariner & Bressay fields. These fields generally contain heavier crudes than Grane, with $12\text{-}14^{o}$ API gravity and viscosity up to 1000 cP. Production is expected to start in 2017, with plateau rates at 55 000 bbl/d for the first three years.

1.4 Extraction Technology

Due to the high density and viscosity of the heavy oil, special extraction methods are needed to recover heavy oil efficiently. The extraction methods can generally be divided in three: Surface Mining, Cold Production and Thermal Recovery Methods.

1.4.1. Surface Mining

Surface mining is a common recovery method of bitumen in Canada. It is applicable when the bitumen is located in very shallow layers over large areas, making it more economical than borehole production. The oil sands are recovered by truck and shovel operations, and transported manually to processing facilities. This method may recover up to 80% of the hydrocarbon, but is controversial due to the large and visible environmental consequences.

1.4.2 Cold Production

Cold production resembles conventional recovery methods, where oil is produced through a borehole without applying heat. It is mostly applied when the oil viscosity is below 1000 cP at standard conditions, or when the reservoir temperature is high enough to mobilize the oil. This method has a lower capital expenditure compared to thermal methods, but the recovery factor is usually fairly low – 6-12% (Oilfield Review, 2006)[5]. Diluents or artificial lift is commonly used to boost well performance.

In Canada, Cold Heavy Oil Production with Sand (CHOPS) is used to increase the production. The bottom-hole pressure in the well is allowed to drop far below the minimum criteria to prevent sand production, which may boost production dramatically, but also means up to 10% sand by volume in the production stream. The removal of sand around the wellbore creates channels in the formation, boosting the production further by creating a growing zone of high permeability. This method requires multiphase pumps and processing equipment able to handle large amounts of solids.

1.4.3 Thermal Recovery Methods

CSS – Cyclic Steam Stimulation

Cyclic Steam Stimulation involves steam injection applied in stages. It is single-well process where the well is alternately acting as an injector and a producer. First, steam is injected for a set time span. Then, injection is halted and the reservoir is allowed to “soak up” the heat from the steam. After the soaking period, the well is set to produce. This cycle is repeated for as long as the well is profitable. It is cheap for a thermal recovery method, and has been shown to give recovery factors up to 40% in Venezuela.

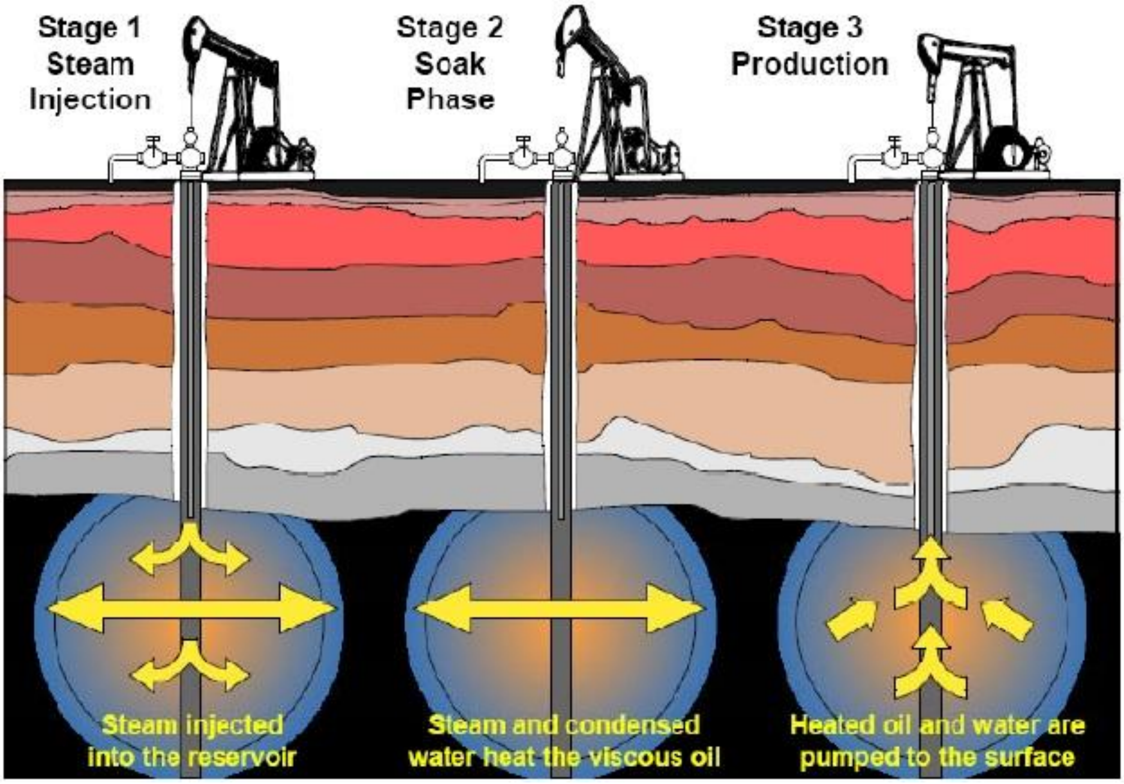

Figure 1.5 – The CSS Process

George R. Scott, (2009)[7]

Steamflooding

This is a multi-well pattern process where injection and production runs continuously. In addition to lowering oil viscosity by supplying heat, the steam injectors provide pressure drive mechanism. The optimum well pattern varies between fields. Recovery factors may be up to 50%, but the method is costly due to the high amount of energy added through the steam injectors. The steam injection rate may determine the success of a project – too high may cause an early steam breakthrough, while a low rate will mean excessive heat losses to over- and underburden.

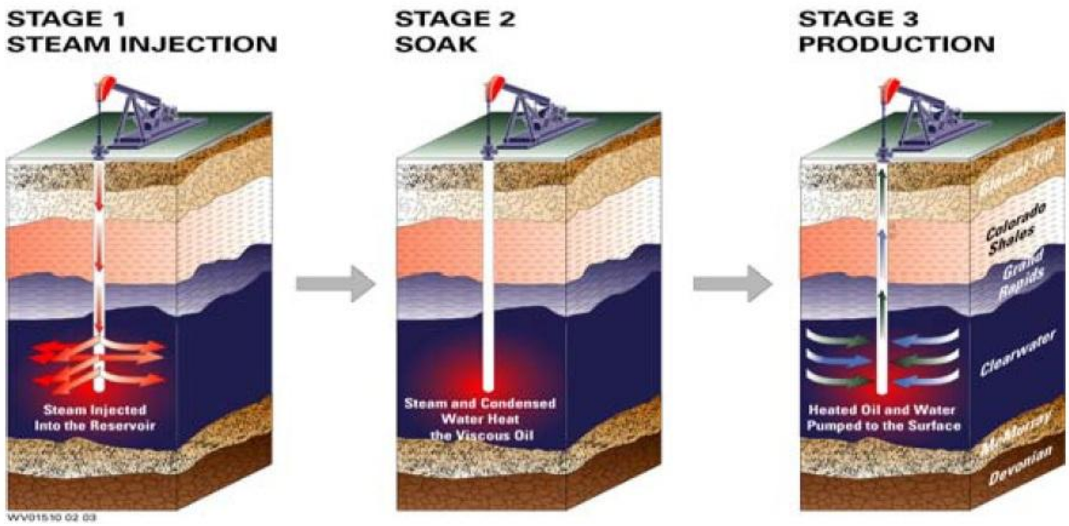

Figure 1.6 - Steamflooding

Stark (2011)[6]

SAGD – Steam-Assisted Gravity Drainage

This method involves the drilling of two parallel horizontal wells in the lower section of the formation. Steam is injected in the upper well, while heated oil and water is produced from the lower. A steam chamber gradually grows above the well pair as the steam rises into the formation, and the oil is heated at the interfacial layer of the steam chamber. This method has been found to be effective for highly viscous oils, and several commercial projects are currently under way. However, SAGD recovery factors are highly sensitive to geology.

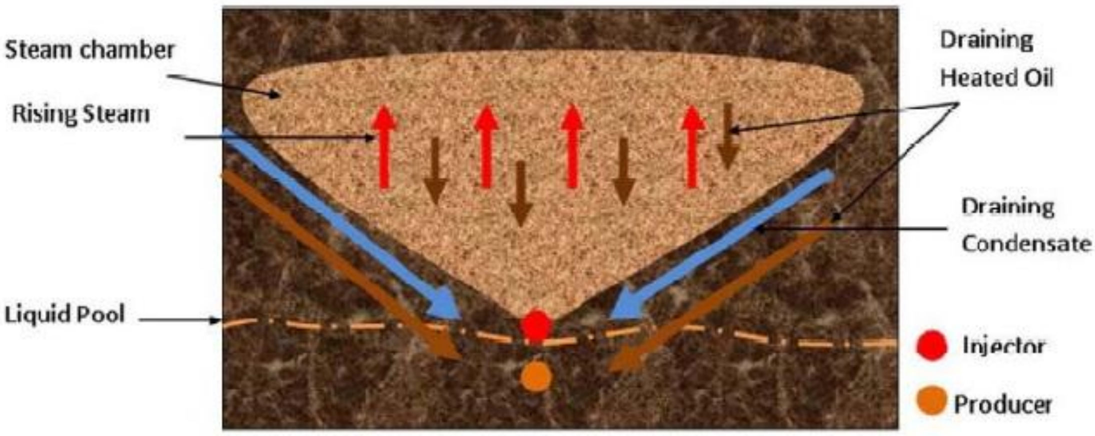

Figure 1.6 – The SAGD Concept

Bahlani & Babadagli, (2009)[8]

2 Heavy Oil Production Technology

This part of the thesis discusses the most common production challenge that heavy oil field developments have to overcome.

2.1 Pipeline Transport

Every drop of heavy oil that is produced goes through some form of pipeline system. However, the special fluid properties of heavy oil provide flow assurance issues that are not found in streams of lighter hydrocarbons. This section discusses why an effective pipe flow of heavy hydrocarbons may be hard to achieve, and presents the most common methods for reducing pressure loss and optimizing the flow conditions.

2.1.1 Viscosity Issues

Heavy oil presents production challenges due to its high density and generally viscous nature. The general equation for pipeline flow is dependent on *density* and *friction factor*:

$$\Delta p = \frac{1}{2} f \frac{\rho}{d} L u^2 \qquad 2.1$$

Where Δp = differential pressure, f = friction factor, ρ = density, d = pipe diameter, L = length of pipe and u = flow velocity.

While the density of heavy oils varies within $\pm$10% of the average, the friction factor may vary by several orders of magnitude. The friction factor is dependent on both density and viscosity, but the relationship changes as the flow regime changes. The Reynold's number is used to determine whether the flow in a pipeline is laminar, transitional or turbulent.

$$Re = \frac{\rho D u}{\mu} \qquad 2.2$$

Where Re = Reynold's number, ρ = density, D = pipe diameter, u = flow velocity and μ = fluid viscosity.

Flow with Reynold's number lower than 4000 is regarded as laminar flow. With heavy oil viscosity in the range of 100-10000 cP, it can readily be shown that pipe flow will be laminar using any economically viable pipe diameter. Figure 2.1 shows the Reynold's numbers for pipe diameters ranging between 1-30 inches, using common heavy oil values for density, viscosity and flow velocity.

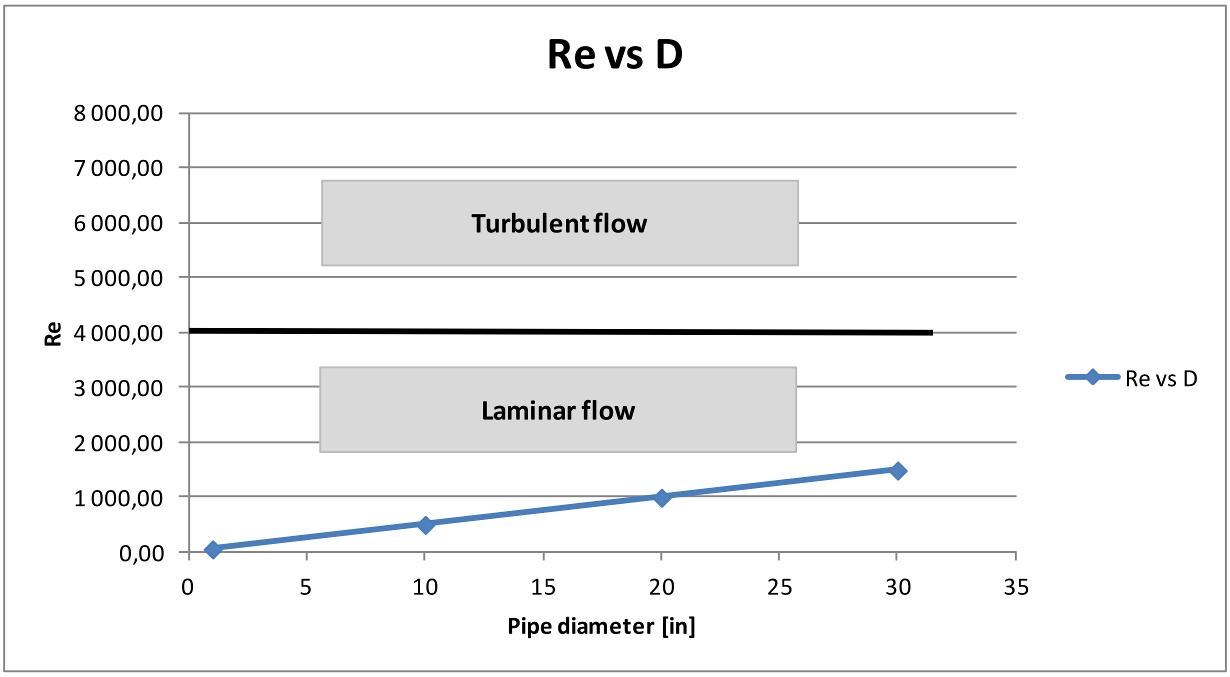

Figure 2.1 – Reynold's Number vs. Pipe Diameter

ρ = 975 kg/m^3, u = 1 m/s, μ = 500 cP

Under laminar flow conditions, pressure drop for a given pumping rate is directly proportional to viscosity, as the friction factor is inversely proportional to the Reynold's number:

$$f = \frac{64}{Re} \qquad 2.3$$

At high viscosity levels, the pressure drop in pipelines may become economically prohibitive, or even prevent flow altogether. Figure 2.2. shows the linear relationship that exists between pressure drop pr. unit length and viscosity. The values are calculated using data from the proposed Keystone pipeline, which will transport heavy oil and bitumen products from Canada to the Gulf Coast of the United States.

The viscosity of heavy oil is exponentially dependent on temperature. The viscosity-temperature relationship of an Athabasca Crude is shown in figure 1.1. It shows that even very heavy bitumen may have viscosity values of only a few cP at high temperatures.

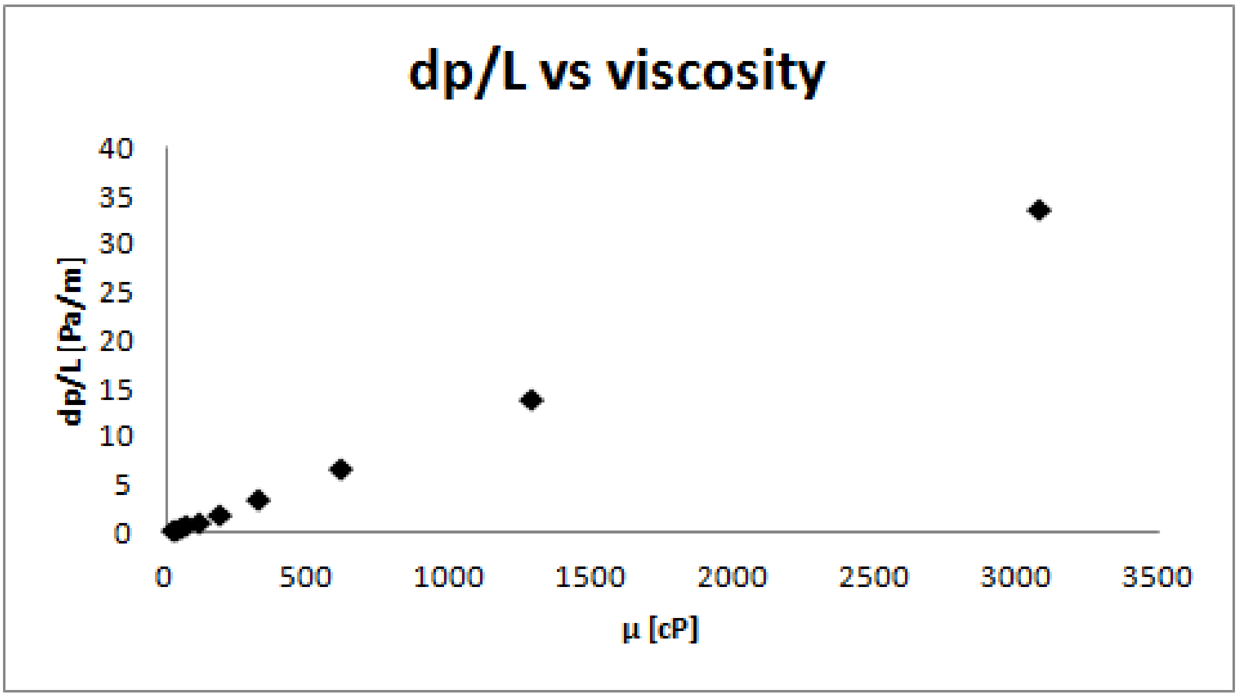

Figure 2.2 – Friction Pressure Loss vs. Viscosity, Laminar Flow

ε = 5,1 µm, D = 30 inches, u = 2 m/s, ρ = 975 kg/m³

Figure 2.2 demonstrate the linear relationship between viscosity and pressure drop for laminar flow. As a rule of thumb, fluids with viscosity values higher than 1000 cP are deemed unsuitable for pipeline flow, as the short intervals between pumping stations would make the construction uneconomic.

2.1.2 Partial Upgrading

The partial upgrading method sends the produced heavy oil into a field refinery that yields a higher-quality, lower density product more suitable for pipeline transport. The upgrading process produces a large unwanted byproduct of coke that has to be handled and deposited. The Syncrude operations in Canada are an example of this, where surface mined 8^o API bitumen is upgraded to a 30-32^o API synthetic blend. It has also been practiced in Venezuela to export extra-heavy oil from the Orinoco belt.

Partial upgrading has the advantage of lower pipeline investments, limited restart issues and no particular corrosions, but the investments associated with a field refinery demands a large production. Potential new techniques for partial upgrading are investigated in section 4 of this thesis.

2.1.3 Dilution

The viscosity of heavy oil may be significantly reduced by blending it with lighter hydrocarbons. This diluent is typically a very light gas condensate (C5+ or “Pentane Plus”). There are two main strategies if a diluent is employed – specifically, the diluent may be recycled or not. In either case, a larger pipeline diameter is needed, as the diluent will command a significant hold-up. For bitumen, diluent may constitute up to 50% of the exported blend.

If the diluent is not recycled, a steady supply of light hydrocarbons is needed. This may be acquired from neighboring conventional oil fields that the company owns, or from a competitor which could prove costly. This strategy assumes that a diluent is even available, something that may not be the case at peripheral heavy oil fields.

If a recycling strategy is chosen, the project economics are less of a subject to the price of diluent. However, additional capital expenditure is required, as a separator facilities and an extra pipeline for the return of diluent to the production site have to be constructed.

Partial upgrading and dilution may be used in different stages of a project. In the Orinoco field developments in Venezuela, the heavy oil is diluted at the production site for pipeline transport to a centralized refinery. At the refinery, the heavy oil goes through and upgrading process for further transport, while the diluent is separated from the blend and returned to the production site for recycling.

2.1.4 Heating

Due to the strong viscosity-temperature relationship of heavy oils, heat generation and retention are used to assure flowing conditions in the pipelines. The costs of insulated pipelines or installing heaters are less than that of dilution or upgrading. However, the pipeline is vulnerable to shut-in periods, as the flowline temperature will approach the surroundings and the entire pipeline could be left immobile. If this happens, a heated diluent will have to be injected to restart flow in the pipeline. (Guevara et al, 1997)[3]. In warmer climates where the ambient temperature does not bring the heavy oil below the pour point, electrical heating may be used to boost production without the need for special restart procedures. This has been demonstrated on shorter production lines in Colombia (Jaimes et al, 2013)[9].

2.1.5 Oil-in- water systems

Oil-in-water emulsions have been used to transport heavy hydrocarbons in Venezuela since the 1980’s. With this technology, chemical additives are used to suspend and heavy oil or bitumen in the water, in the form of micro spheres. This may greatly decrease the apparent viscosity of the heavy oil. To assure a stable emulsion, it is important to select a chemical that is effective at varying conditions.

2.1.6 Core-annular flow

Core-annular flow injects water into the pipeline to form a coating around a core of heavy oil. This technology may potentially reduce friction pressure loss in the pipeline to that of volumetrically equal pure water flow. It is discussed in section III of this thesis.

2.1.7 Manual transport

For some operations, transport by truck, rail or barge may be the most economic alternative. The wells then produce into a storage tank, which is emptied at regular intervals. This is typically done for low-rate wells located a good distance from any processing facilities, when investments in pipelines and flow assurance technology would be too expensive.

2.2 Solid precipitation

2.2.1 Asphaltene

Asphaltenes are high molecular weight hydrocarbons, arbitrarily defined as a class of petroleum insoluble in light alkanes but soluble in toluene or dichloromethane. Asphaltenes have been known to cause flow assurance problems in conventional oil production. These effects include:

- Pipe flow area reduction
- Increased friction pressure loss
- Wettability alteration
- Pipeline blockage
- Reduced efficiency of production equipment

All of these effects are related to the asphaltenes precipitation due to decreased solubility in the produced fluid. This may occur under changing pressure/temperature conditions.

Heavy oils are known to have high asphaltenes content, but as asphaltene solubility is proportional to the molecular weight of the components, they are less vulnerable to asphaltene precipitation than lighter fluids. However, the asphaltene has a tendency to aggregate, making the oil very viscous. A common flow assurance strategy is diluting the heavy crude with lighter hydrocarbons, either an injection fluid or another wellstream, thus reducing viscosity and friction pressure loss. This will change the composition of the fluid, and asphaltene may be destabilized and precipitate.

Chen et al (2010) showed that asphaltenes may precipitate in heavy oil pipelines depending on pressure and temperature conditions. It is necessary to consider these issues in the flowline design, especially scenarios where heavy oil is blended with lighter diluents.

2.2.2 Hydrates

Hydrate formation in heavy oil streams has not been extensively studied in the past. Given that steam injection is the primary method of heavy oil recovery, many pipelines transporting heavy crude will carry a sizeable fraction of water. Although the operating temperature is often kept as high as possible to keep the viscosity low, shut-in scenarios could mean that the pipeline will cool off into the hydrate region.

Shell ran a series of tests to investigate the potential of hydrates forming in a heavy oil production line (Mehta et al, 2004)[13]. First, the complete phase boundary of a heavy was studied, and compared with in-house hydrate prediction tools. The results proved that hydrate plugs can and do form in heavy oil flowlines under the right conditions. Specifically, the transitional period from a shut-in to flowing state is where hydrates are most likely to form. Consequently, operability strategies need to include plans to ensure that the pipeline will not fall into the hydrate formation region in the event of a long-term shut-in.

The “good” news is that viscosity management criteria for heavy oils often are a lot stricter than the hydrate formation criteria. This means that the measures you would need to prevent hydrate formation are implemented by default for a heavy oil production project.

2.2.3 Scaling

The precipitation of calcium napthenates both in reservoir and production systems are known to be a problem when recovering heavy oil (Mohammed, 2010)[13]. These issues may escalate when sea water is injected into the reservoir, changing salt concentrations and pH levels of the liquids. In conventional reservoirs, this is normally prevented by the injection of an inhibitor, but the low mobility in a heavy oil reservoir may prevent this. This is not a topic that has been extensively studied, but its’ potential impact is greatly dependent on the conditions and fluid composition of each reservoir.

2.2.4 Wax

Wax deposition causes flow instability in the production of many conventional oil fields. This is caused by precipitation of paraffin in well tubing or flowlines. Heavy oils, however, are in most cases highly biodegraded, minimizing paraffinic content. For this reason wax is largely a non-issue in heavy oil production.

2.3 Pumps

Pumps are necessary for the transportation of oil from wellsite to central facilities, between upgrading installations and for long-range transport to other distribution centers.

Three parameters are critical in the selection of heavy oil pumps:

- Oil viscosity

- Solids production
- Presence of gas in produced liquids

There are two common categories of oil pumps used in the industry: positive displacement pumps and dynamic pumps. Viscosity will affect the performance of all pumps, but in different manners. With a positive displacement pump, oil up 100’000 cP viscosity may theoretically be pumped, though the realistic limit for pipeline transportation of oil is at ~1000 cP. Dynamic pumps generally become unattractive for oil viscosities above 100 cP. For this reason, positive displacement pumps are usually preferred for heavy oil applications.

Heavy oil may have significant solids content, and this must be considered when selecting pump. The suspended solids will increase the apparent viscosity of the fluid, but more important are the eroding and depositing effect they might have. This may reduce the lifetime of a pump down to a few months. Effects may be mitigated by either installing sand removers upstream of the pump, or select a low velocity pump such as twin screw pumps.

High viscosity makes separation of heavy oil difficult, and some associated gas often remains in the stream. This may significantly impair the performance of conventional pumps.

In California, twin screw pumps have successfully been used in heavy oil thermal applications since the 2000’s (Saadawi, 2012)[11].

2.4 Offshore

Offshore heavy oil fields face additional challenges compared to onshore production. The offshore setting implies added costs and platform space constraints, and this makes traditional heavy oil production methods like steam injection unsuitable. For this reason, offshore heavy oil recovery is limited to cold production, with some secondary recovery methods like water and gas injection applied. This has consequences for the production processes, as low temperature at the wellhead will significantly increase viscosity and limit flow rates.

Brazil has seen extensive discovery and development of offshore heavy oil fields, and oils with API gravity between 14 and 19^{o} API make up 26% of the proven volumes (Trevisan et al, 2009). Petrobras has initiated several research programs to improve and optimize production technology (Trindade & Branco, 2005)[12].

Much has been done to investigate artificial lift technology for heavy oils. This is even more important for heavy oil fields, as the onshore production boosting techniques may not be viable. Gas lift completion shows better cost/benefit ratio than electrical submersible pumps in conventional deepwater fields. For heavy crudes, the effect of gas lift is limited due to high viscosity, but submersible pumps have a high rate of failure.

Producing viscous oils may significantly change the water-oil ratio over the life of the well. This has the potential to both boost and limit flow rates. If an oil-in water emulsion or dispersion is achieved, it is generally seen as favorable, as this will reduce the pressure drop in a flowline. However, shear forces from pumps or restrictions may cause the emulsion to revert to a water-in-oil emulsion, which will have a greater viscosity than the crude itself. Also, either of these emulsions may cause processing problems, as the separator will struggle to separate the phases. This is usually solved by injecting a demulsifying agent into the production stream, but the chemical consumption rates for heavy oil-water emulsions may be much quite high, and thus cost may be prohibitive. It is important to understand the emulsion mechanisms of a potential heavy oil project, in order to implement the correct flow assurance strategies.

Due to the limited platform capacity and limited subsea technology development, the processing utilities may be the most critical area for development of offshore heavy oil projects. With onshore projects, most of the work has been done using conventional separators, only with increased size to accommodate the additional retention time needed. As this strategy will not be sufficient offshore, new technology is required. Petrobras has initiated research into compact separation technologies such as hydrocyclones and centrifuges.

The high retention time needed for heavy oil separation is related to the high oil viscosity. This may be partially mitigated by installing heaters upstream of the separator facilities. If the oil is heated to 140^{o}C, conventional separators may be used. (Mehta et al, 2004)[13]

3 Core-Annular Flow

3.1 Concept Introduction

The aim of core-annular flow is exploiting the low viscosity of water and high density of heavy oil to transport the heavy crude with a much lower pressure loss than what you would normally see. This is done by introducing a flow of water into the pipeline at its head. Somewhere further down the pipeline, they two liquids will stabilize into a concentric flow pattern, where the heavy oil flows in the center of the pipe while the water occupies the rim. The water acts as a lubricator as long as the core of heavy oil remains stable. The result of this

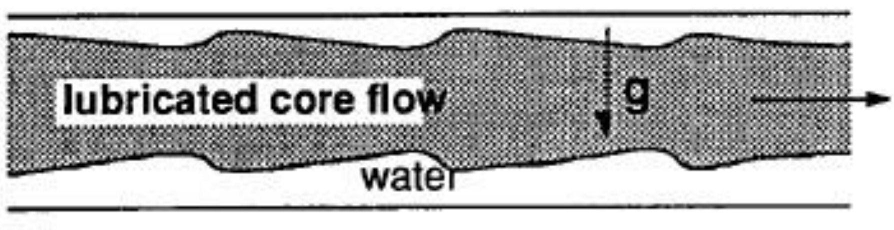

Figure 3.2 – Core Annular Flow Sketch

Joseph et. al (1997)

is friction pressure loss that resembles an equal volume flow of water.

The first evidence of using water as a lubricant for oil is found in a patent application by Isaacs & Speed in 1904. Since then, it has drawn interest and been the subject of extensive research and testing, as it is a production method that doesn’t require more than the horizontal injection of water into the pipeline to work in theory.

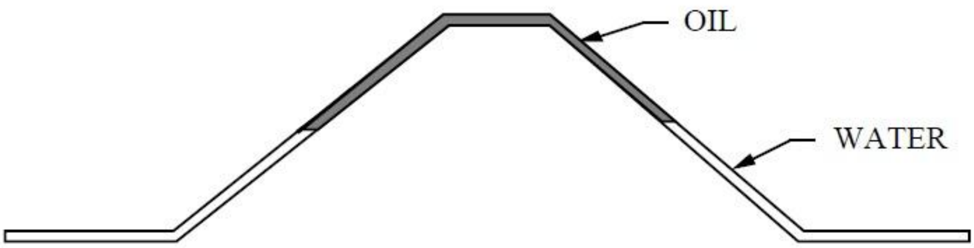

Fig 3.2 – Shut-in Issues faced by Core-Annular Flow

In spite of this, commercial core-annular flow projects have been few and far between. The reason for this is that while CAF may greatly decrease pressure drop in a steady-state scenario, problems emerge the moment flow rate drops or the pipeline is shut in. The flow regime will no longer be stable, and the liquids will segregate into two horizontal layers. If the pipeline has an elevated section, this could lead to a permanent heavy oil plug blocking the flow.

3.2 Experimental Studies

Brannwart & Prada (1999) tested core flow technology for applications in Brazil's deepwater heavy oil fields. Using a 1" galvanized steel laboratory flow loop, they found that core annular flow could decrease total pressure loss by a factor up to 150. They suggested applying core annular flow to heavy oil lifting both in subsea flowline and well for increased flow rate, but noted the need for subsea separation systems. Flowline restart issues were not discussed.

Peysson et al investigated the start-up pressure requirements for starting up a CAF flowline after a shut-in period. They employed a 16^o API heavy crude of moderate viscosity (4750 cP @ T= 19^oC). They found that the greatest viscosity reduction was achieved with a low pipeline temperature, indicating that the core-annular flow stabilizes more easily when there is a large viscosity difference between the water and the oil. The maximum pressure drop reduction achieved was 98%.

After shorter shut-in scenarios of 10-60 seconds, the restart pressure drop was found to be about 50% of the pressure drop without CAF. While this is a substantial decrease, it would need to be improved for industrial application.

In order to reduce the restart pressure, the wettability of the lubricating water was changed by adding salts to the solution. This eliminated the restart pressure for production stops shorter than 60 seconds. However, such short stops are rarely encountered in the field. A more realistic and longer production stop of 600 seconds resulted in a restart pressure close to the pressure without core-annular flow.

These results indicates that while core-annular flow can greatly decrease pressure loss in a heavy oil flowline, the restart pressures required are too large to make it an effective industrial technology. Advancements will have to be made in decreasing the restart pressure, likely either by adjusting the pipe wall properties or through a low-concentration additive to the water.

3.3 Commercial application:

In spite of being a well-known technique for pressure loss reduction in pipeline transport of heavy oil, only a few commercial projects are known. One of the reasons for this is the difficulty in starting up the correct flow regime in large diameter pipes (Poesi et al, 2006). It has also been shown not to be effective for less viscous oil streams (μ<500 cP), thus limiting it to the less common extra heavy oil pipelines.

The most cited example of successful application is the 8-inch, 38,6 km Shell pipeline from North Midway Sunset Reservoir (Bakersfield, California) to the central facility at Ten Section (Joseph, 1997). Here, both fresh and produced water were injected into the pipeline to maintain a 30% water fraction for core-annular flow for 5 years. The flow rate was relatively constant at 24 000 bbl/d, with pressure drop varying between 900 and 1100 psia.

When fresh water was replaced with produced water, pipeline fouling was found to decrease and flow conditions stabilized. This was explained by the natural chemical content of the produced water, that included 0,6 wt% of sodium metasilicate.

Using fluid data from the Midway Sunset field and assuming a constant flowline temperature of 50 ^{o}C, a friction pressure loss comparison was made using basic one-phase flow equations. The results are presented in table 3.1. They show that the friction pressure loss for heavy oil is ~15 times that of core annular flow. This shows that core annular flow was an effective measure for minimizing pressure loss, bringing it quite close to the friction pressure loss for pure water.

	Density [kg/m3]	Viscosity [cP]	Δp_f [psi]
Heavy Oil	992	4800	14179
Water	1000	1	527
Core Annular Flow	994,4	-	900

Table 3.1 – Pressure drop for different flow scenarios

At Lake Maracaibo in Venezuela, core-annular flow is used to transport heavy oil from well clusters to process facilities (Nunez et al, 1998). Here, the wellstream contains approximately 16% water. Fresh water is pumped into the flowline to catalyze core-annular flow regime, taking the total water fraction up to 20%. The flow has been shown to be relatively stable, and any fouling build-up is flushed out by temporarily increasing the water fraction.

Syncrude has taken advantage of a similar phenomenon in their transport of bitumen from wellhead to upgrading facilities (Sanders et al, 2004). The oil is produced by a hot-water extraction process, and the product known as a bitumen froth is a stable emulsion of 60% bitumen, 30% water and 10% solids. When the froth enters the pipeline, water disperses from the froth and forms a lubricating layer surrounding the emulsion core. This decreases pressure gradients by several orders of magnitude from what would be expected based on the viscosity of the froth. It is an economically attractive option for transport, as it does not require any additives or energy input.

Core flow was successfully applied during the recovery of heavy fuel oil from a sunk tanker offshore Spain in 2004 (Berenguer et al, 2005). Repsol used core flow to transport fuel from a shuttle, through a riser and onto an FSO unit, effectively reducing frictional losses by two orders of magnitude. They recognized problems restarting the flow after shut-downs, and found that this could only be done by flushing the riser with diesel.

3.4 Future applications:

Commercial projects utilizing core-annular flow are dependent on a resolution to the substantial restart pressure. Every project or lab experiment undertaken shows that when flow is halted for a significant time, the fluids in the pipe will stratify, resulting in a large increase in friction pressure loss that could prevent a successful restart of the flow. Such an event will have dire economic consequences, and this holds companies back from applying core-annular flow in their projects.

Several investigations have been made in the past decade to resolve the restart problem. Peysson et al (2005) found that adding salts to the water delayed the stratifying process, but did not help for longer shut-in periods. A patent submitted by Peysson et al (2009) to the United States Patent Application Publication suggests a yield stress additive to the injected water that would prevent stratification during shut-in. No publication verifying the success of this method has been found. This would also implicate new issues, such as corrosion and costs related to continuous additive injection.

Arney et al (1996) looked into reducing the adhesion of heavy oil to the pipeline wall by changing the pipe material. They hoped to reduce fouling of the pipeline wall and limit restart pressure. They found that fouling could be completely prevented by using a cement-lined pipeline. This also shortens the time needed to achieve core-annular flow conditions after a restart. However, they did not find a solution for preventing oil blockage at the top of inclined pipeline sections. Poesi et al (2006) developed an analytic model of the stratified-restart scenario. They concluded that restart pressure increased with increasing water hold-up, and decreased with decreasing oil viscosity.

To conclude, the blocking of elevated pipeline sections during shut-in limits the potential of core-annular flow as a feasible flow assurance strategy. Until this is issue is resolved, core-annular flow is likely to be limited to shorter, horizontal segments and academic studies. As the potential for increased flow is great, it is suggested that work is initiated to develop a solution.

4 Adjustment of Heavy Oil Properties by Addition of Nano-Sized Metal Particles

This part of the thesis discusses a set of laboratory experiments, where nano-sized metals were added to heavy crude for the purpose of viscosity reduction. Similar experiments have previously been conducted by Shokrlu & Babadagli (2010)[21] and Greff & Babadagli (2011)[22], where the nano-sized metals were introduced to catalyze an in-situ upgrading of the heavy oil for increased recovery. Our experiments investigate whether they may also be applied effectively at atmospheric conditions, in order to reduce the viscosity of produced oil and thereby reducing friction pressure loss in the pipeline.

4.1 Background – Wellsite Upgrading and Viscosity Reduction

Transport of heavy oil from the wellsite to refinery can be technically and economically challenging. The low API density and high viscosity means additional capital expenditure in terms of increased pipeline dimensions, insulation and frequent pumping stations. These factors will limit distance of wells from the central processing facilities, and may potentially prevent the construction of a pipeline altogether.

A common strategy is to dilute the heavy crude using naphta or condensate (Fukuyama, 2010). While effective in improving the flow properties, this method can be very costly depending on the price and availability of the diluent. The volume of diluent added may be up to 30% of the final well stream. Also, this strategy demands the construction of two separate pipelines, adding substantially to capital expenditure. If facilities for the upgrading of heavy crude could be implemented at the wellsite, it might make previously unprofitable projects feasible.

Processes such as thermal cracking, solvent deasphalting and hydrocracking are commonly used for the processing of heavy oil at conventional refinery configurations. They are not well suited for upgrading of heavy crudes at wellsites for the following reasons:

- *Thermal cracking:* This process leaves a large mass of byproduct from the coker, which requires complex handling and facilities.
- *Solvent de-asphalting:* Asphaltene components are separated from the deasphalted crude stream, without substantial upgrading taking place.

- *Hydrocracking:* The catalyst employed is subject to active degradation, and the process requires extensive capital expenditure in high-pressure equipment, a hydrogen production unit, and a source of hydrogen.

The consequence of these issues is that at-wellsite upgrading technology is not yet economically and logistically feasible. This justifies the investigation of new upgrading technology , with the potential for employment at the wellsite.

4.2 Use of nano-metals to decrease heavy oil viscosity by aquathermolysis

The term aquathermolysis describes chemical reactions first discovered during steam stimulation of heavy oil reservoirs. While the objective of steam stimulation is to achieve a temporary viscosity reduction by heating the crude, Hyne et. al. (1984)[14] found that permanent changes were made to the physical properties of the heavy oil. The generally accepted hypothesis is that high-pressure and high-temperature steam is capable of breaking the carbon-sulfur bonds in asphaltenic components of the heavy oil/bitumen. The result of this is a reduction of high molecular weight components, thus permanently reducing the viscosity of the oil.

Clark et. al. (1990)[15] found that the aquathermolytic reactions could be catalyzed by the presence of aqueous metal species. When first-row transition metals were added to the steam-oil mixture, the viscosity reduction of the heavy oil was significantly amplified. Maity et. al. (2010)[17] confirmed the results in the lab, and also presented a field test from the Liaohe oil field in China, where viscosity of the crude was reduced by 80%. Such a reduction would significantly impact both reservoir flow and pipeline pressure loss.

Fan et. al (2004)[18] studied the effect of reservoir minerals on the composition of heavy oil during a steam stimulation process. A mixture of heavy crude, water and oil was conventionally heated in an autoclave from 160 ^{o}C to 240 ^{o}C over a period of 48 hours. The presence of reservoir minerals during this process was found to decrease viscosity, increase saturate and aromatic content while decreasing resin and asphaltene content. Later, Li et al (2007)[19] applied a nano-sized nickel catalyst to a mixture of oil and water, by suspending the nickel in a microemulsion. The sample was heated to 280 ^{o}C and kept at 6,4 MPa pressure for 24 hours. They achieved a significant viscosity reduction when the catalyst was present, compared to running the same process with pure water.

Hascakir et. al. (2008) added micron-sized iron powder to heavy oil, without the presence of water. Surprisingly, they found the viscosity to decrease by this simple addition of catalyst, even without the presence of steam. Shokrlu & Babadagli (2010)[21] attempted to recreate their results, but while they were able to reduce the viscosity for certain samples, the effect was far lower than what Hascakir et. al. reported. Nevertheless, they were able to verify an optimum concentration of catalyst for viscosity reduction.

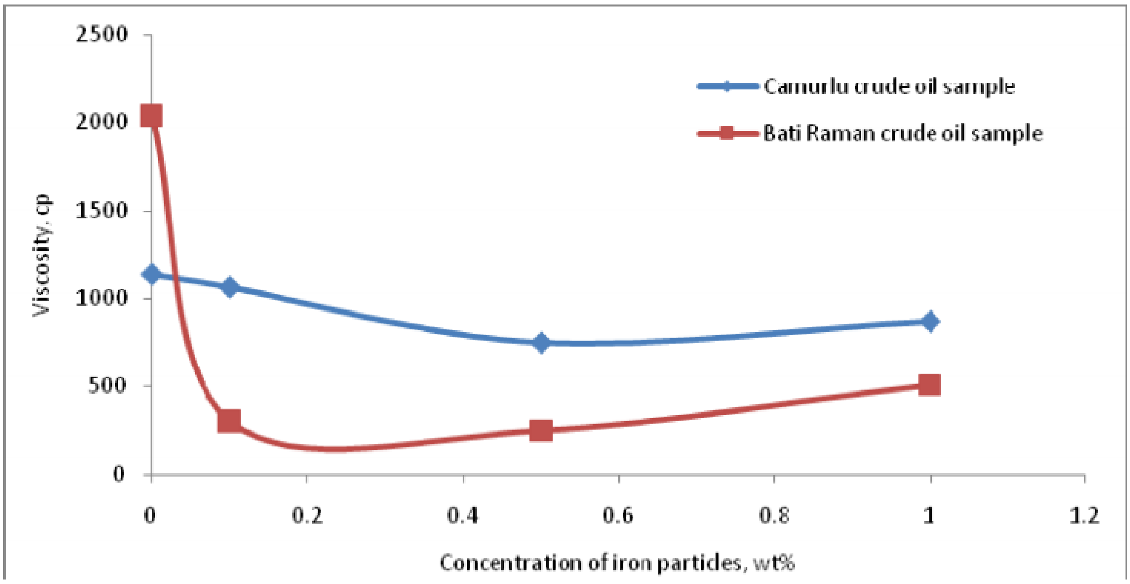

Figure 4.1 – Viscosity Effect of Iron Catalyst – Hascakir et.al. (2008)[20]

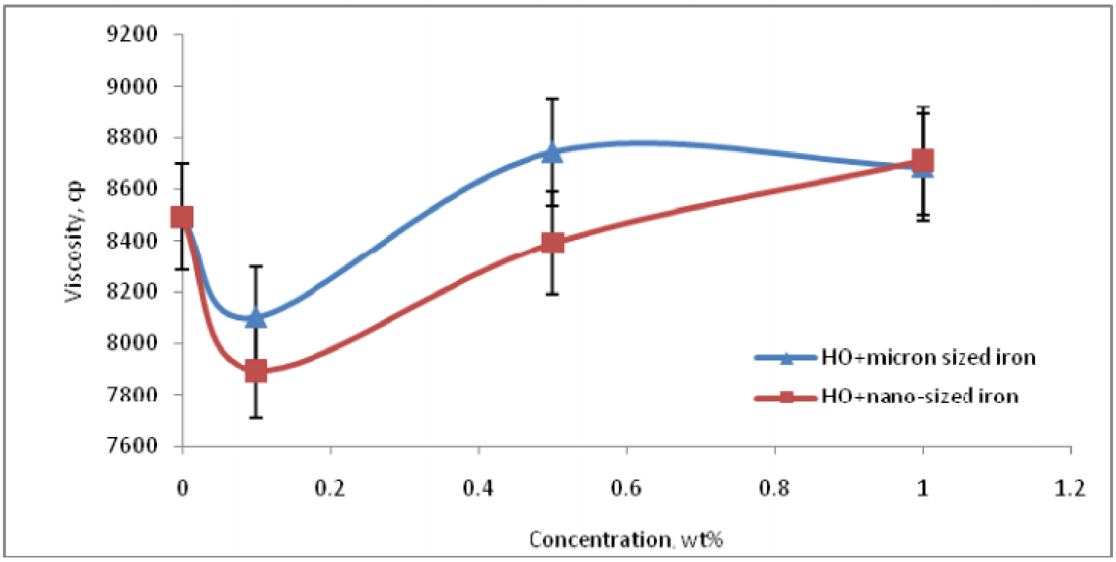

Figure 4.2 – Viscosity Effect of Iron Catalyst – Shokrlu & Babadagli (2011)

Greff & Babadagli[23] (2011) exposed heavy oil mixed with different nano-sized metals to microwave radiation, using a domestic microwave oven. Their goal was to achieve an effective aquathermolysis without the presence of steam, using the photochemical reactions of microwaves to create reactive hydrogen radicals, which would act as hydrogen donors for the aquathermolysis reaction. They observed a viscosity reduction when metal concentration was kept low, but at higher concentrations the viscosity increased. This was suggested to be due to an increased vaporization, caused by the cracking of asphaltene components.

4.3 Purpose of Experiments

Two experiments were conducted to investigate the feasibility of nano- and micron-size metal particles in the upgrading of heavy oil, for the purpose of viscosity reduction. While such investigations have previously been made, the effects reported have varied greatly, and it has not been investigated with surface processing in mind. For this reason, it is important to determine whether this technology may have a future in heavy oil production. Our experiments were designed to answer the following critical points:

- Although Shokrlu & Babadagli[21] reported a viscosity reduction when nano-sized metals were added to heavy oil, it was not as effective as reported by Hascakir (2008)[20], and far from effective enough to validate industrial use. Our experiments seek to clarify whether nano-sized metals can give meaningful reduction to heavy oil viscosity without the presence of water.
- Greff & Babadagli[22] reported that the presence of nano-sized metals during microwave heating could catalyze upgrading reactions and decrease viscosity. We investigated the effect different types of metals had on the oil viscosity, using iron, copper, nickel and zinc. We also sought to clarify the effect of particle size by using both nano- and micron-sized copper.
- Greff & Babadagli found that a substantial amount of heavy oil would evaporate when heated by microwaves. This seemingly explained why high concentrations of nano-sized metal led to higher viscosity measurements. However, there is a discrepancy in that lower concentrations of metals lead to a net viscosity reduction, compared to the base case without metal content. We looked into the relationship between metal concentration, viscosity and vaporization to see if their results could be reproduced.

With these objectives in mind, two sets of experiments were conducted. In the first set of experiments, nano- and micron-sized nano metals were dispersed in untreated heavy oil. The viscosity was then measured, to investigate the effect of the catalyst at atmospheric conditions. The second set of experiments exposed the mixed heavy oil and catalyst to microwave radiation.

4.4 Experiment #1

Investigating Heavy Oil Viscosity Reduction by Addition of Nano-sized Metals

In our experiment, hydrophobic nano-sized metal particles were added to a base fluid for the purpose of investigating how heavy oil viscosity may change when metals are introduced to the mixture.

Our hypothesis is that the presence of nano-sized transition metals in the heavy oil will permanently alter the composition and reduce the viscosity of the oil through catalytic reactions, even without any steam stimulation. This was documented by Hascakir et. al (2008)[20], but could not be fully reproduced by Shokrlu and Babadagli (2010)[21].

4.4.1 Experimental details

Samples

The base fluid consisted of 90% Athabasca bitumen crude, and 10% n-dodecane. This is done to make the sample manageable at room temperature, while maintaining the heavy oil properties. While minor variations were observed between the samples, the average viscosity was found to be 8500 mPas at 25 ^{o}C. The API density was measured to be 12^{o}, which would make it similar to heavy oil bordering to bitumen.

Heavy Oil Data		
Fluid	**Viscosity @ 25 ^{o}C [cP]**	**API gravity**
Bitumen	100000	8,2
Dodekane	1,34	58,6
Sample mix	5839	12,0

Table A.1 – Sample properties

Catalyst

In this experiment, nano-sized iron, nickel, zinc and copper was utilized. Additionally, micron-sized copper was used to determine the effect of specific surface area. The basis for selection of these catalysts lies in the fact that they have previously been used in several other studies, making comparisons simpler. Also, they are not among the most expensive nano-metals, and this is important as the price pr. gram of catalyst will be a critical factor for any industry project.

The particle size and purity of the catalysts were verified using a Scanning Electronic

Catalyst properties			
Nano metal	**Particle size**	**Surface area [m^2/g]**	**Resistivity**
Iron	40-60	6-13	9,71
Nickel	40-60	10-15	6,97
Zinc	40-60	12	5,8
Copper	40-60	12	1,673
Copper	500	3	1,673

Table 4.1 – Catalyst properties

Microscope (SEM). The results from the scans are included in Appendix C.

The nano metal data can be found in table 4.1. Fe, Ni, Zn, and Cu are all first order transition metals, and have previously been shown to have a catalytic effect on the aquathermolysis process. (Clark, 1990)[16]. However, the effect when applying them in nano-size has not yet been clarified.

To ensure that the metals are evenly suspended throughout the fluid, the samples were irradiated by ultrasonic waves for 30 minutes before the measurements were started.

4.4.2 Procedure:

1. 10 gram of n-dodecane and 90 gram of bitumen is mixed using a combined heater and magnetic steerer.
2. 0,1 / 0,5 grams of nano metal are added to the sample.
3. The sample is put in a ultrasonic bath for 30 minutes to prevent aggregation.
4. A sample is taken from the beaker glass, and measured at T = 21, 25, 35, 50, 65, 80, 100 ^{o}C. Measurements are taken using a Brookfield LVDV-II+ Pro Viscometer. Shear rate is kept between 10 and 25% of the viscometers capacity for accurate measurement. For efficiency, five samples are measured in the same sequence.

4.4.3 Results and discussion:

The results from the viscosity measurements for each sample are presented in Table 4.2. The measurements for each sample were repeated three times to confirm the results and eliminate erroneous data. The data presented here are the arithmetic average of the measured values for each sample at each temperature. To test the repeatability of the viscometer and the procedure, several tests were conducted using the crude mix without additives. The repeatability was found to be good, with an average variance of 1,1% between the temperatures. The data is presented in Appendix A, Table A.1.

Sample	Concentration of particles, wt%	Viscosity [cP]		
		25 °C	50 °C	100 °C
Base mix	0	5825	755,0	54,7
Nano Iron	0,1	7738	989,8	71,9
	0,5	5879	779,8	59,6
Nano Nickel	0,1	6059	806,5	56,3
	0,5	6899	884,5	64,1
Nano Zinc	0,1	6749	999,8	62,7
	0,5	6839	876,8	63,5
Nano Copper	0,1	6749	865,3	62,7
	0,5	6869	880,6	63,8
Micron Copper	0,1	5969	765,3	55,4
	0,5	5954	773,0	58,1

Table 4.2 – Viscosity measurements

Figure 4.1-4.3 shows the relationship between viscosity and metal concentration at each temperature for each sample. It is evident that none of the samples exhibit decreased viscosity when compared to the base case. Several attempts were made to remedy this, including making changes to the procedure, but the results were always consistent with what we see in figure 4.1-4.3.

Both nano- and micron-sized copper has been investigated for the purpose of determining the effect of surface area of the powder. As neither is able to decrease the viscosity, this point is rendered somewhat moot, but it is interesting to observe that the micron-sized copper sees a much smaller viscosity increase than the nano-sized powder.

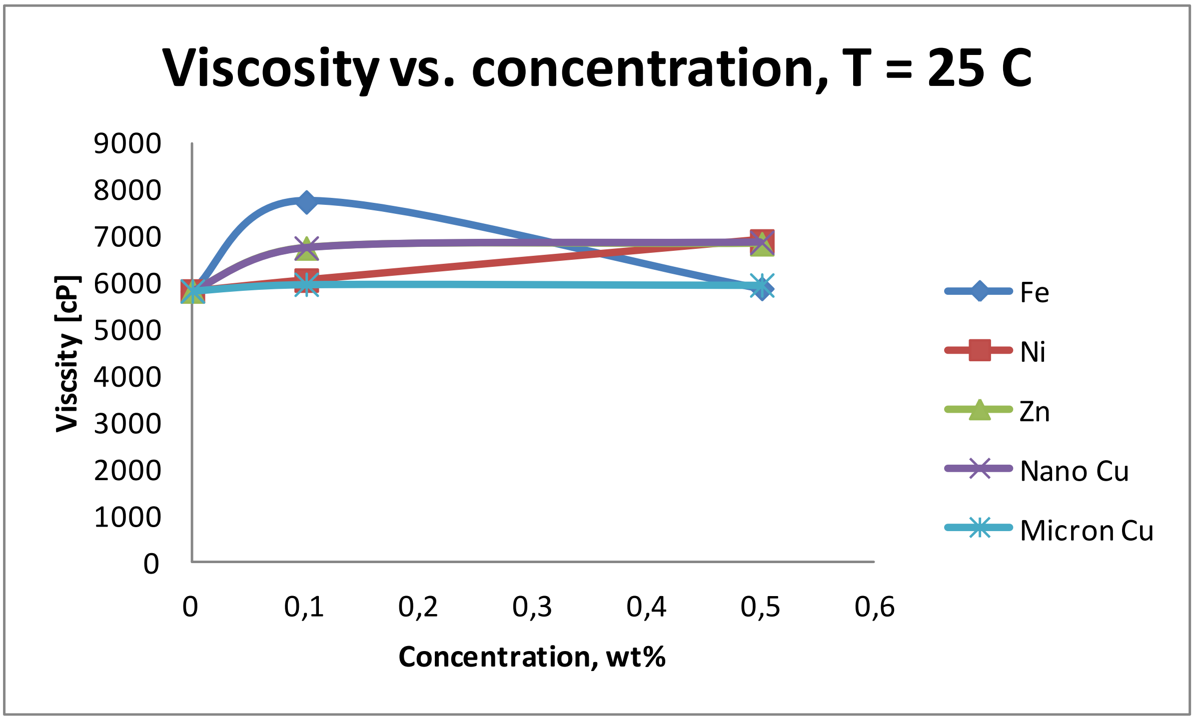

Figure 4.1 – Viscosity vs. Catalyst Concentration, T = 25°C

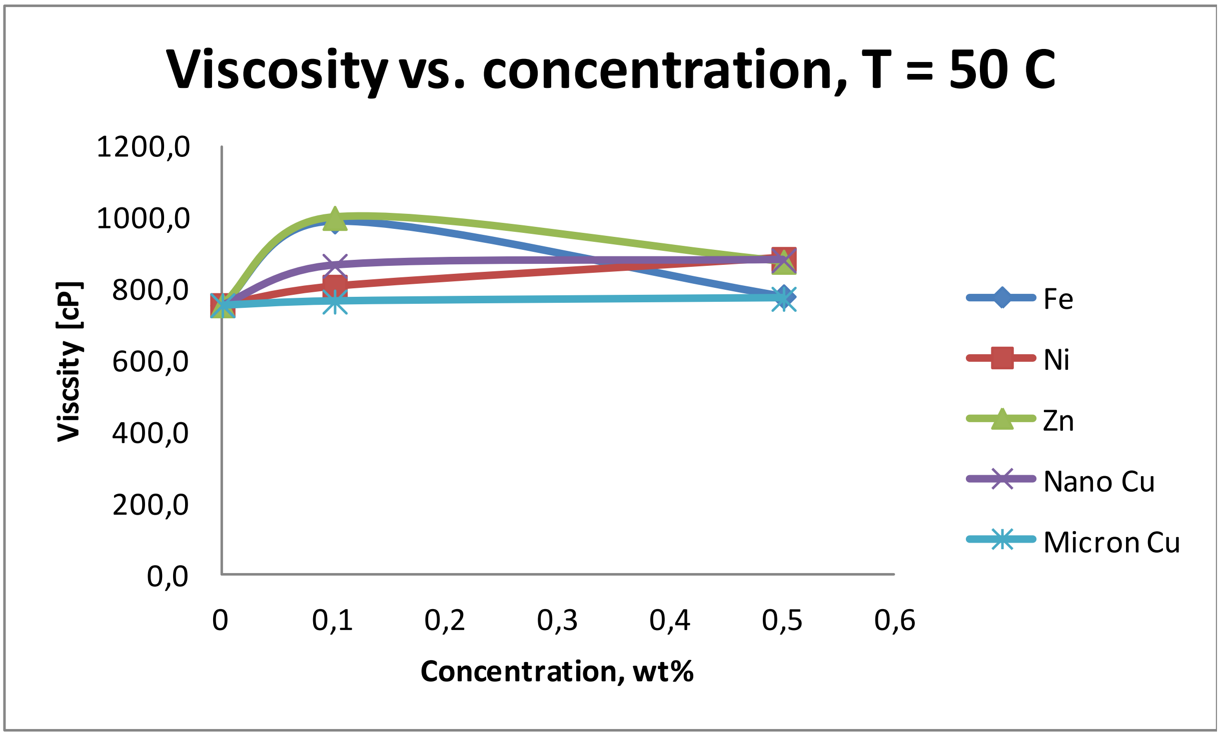

Figure 4.2 – Viscosity vs. Catalyst Concentration, T = 50°C

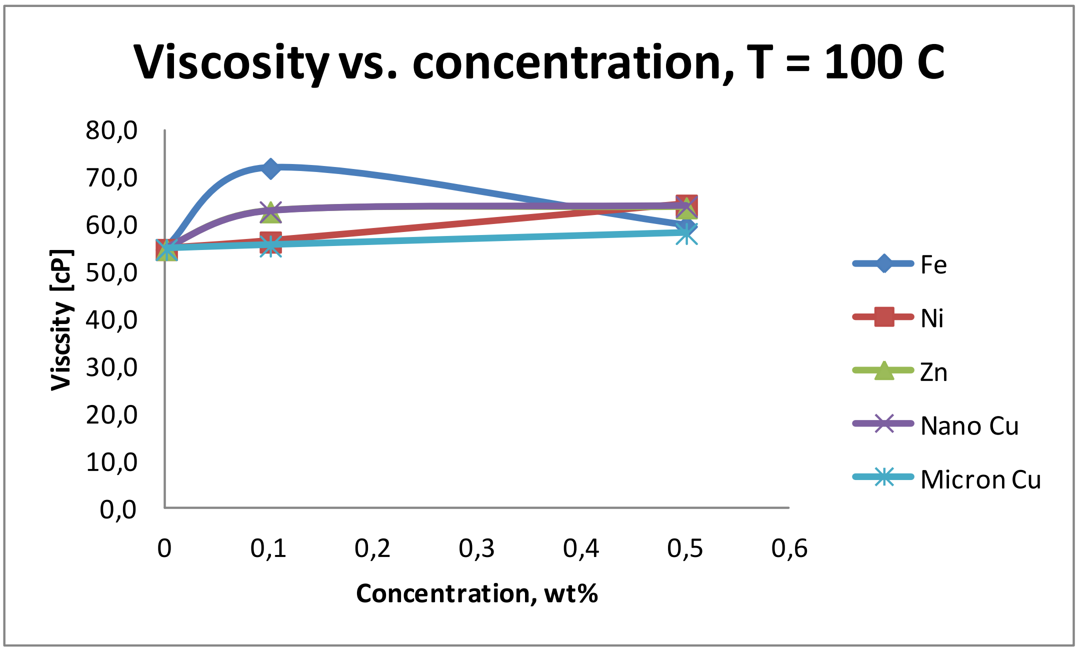

Figure 4.3 – Viscosity vs. Catalyst Concentration, T = 100°C

This study was based upon the results presented by Shokrlu et. al. (2010)[21], who in turn were inspired by Hascakir (2008)[20]. Figure 4.1 and 4.2 display the results from their studies for a 0,1 wt% concentration of an iron nano-catalyst. It is clear that Shokrlu achieved results that correspond better with ours. Upon further review, Hascakir's data were based on a 2006 conference paper from the same author that is not available to the public. For this reason, it has not been possible to investigate and compare their methodology with ours.

Shorklu (2010) made several suggestions for the lower viscosity reduction in his investigations. In addition to the catalytic aquathermolysis reactions, other reactions such as the rusting reaction may occur when the iron nanometals interact with the heavy crude:

$$4\,Fe(s) + 3O_2(g) + xH_2O(l) => 2Fe_2O_3 + \; xH_2O(s) + \; 1644\;kJ$$

This is normally a slow reaction, but may be accelerated by acidic components of the heavy oil. It cannot be ruled out that this has affected the measurements of Hascakir (2008), if the heavy crude investigated was particularly acidic. Our samples may also see the viscosity reduction inhibited by the formation of complex molecules as the iron reactions progress. Yet another factor is the asphaltene content, which was at 29% in the Bati Raman sample investigated by Hascakir (2008)[20]. This may have contributed to the large viscosity reduction they obtained.

Our conclusion is that no viscosity reduction was observed when nano- and micron-sized transition metals were added to the heavy oil mixture. On the contrary, viscosity is observed to increase as the metal is added to the samples. This is observed for all types of most likely reason is the lack of a hydrogen donor for the catalyst reaction to take place. We observe that conventional heating up to 100 ^{o}C has no permanent effect on the viscosity of the samples.

The addition of nano-sized metals alone for the purpose of heavy oil viscosity reduction is not judged to be a feasible strategy.

Sample	Maximum viscosity reduction	Optimum concentration, wt%
Camurlu Crude Oil	34 %	0,5
Bati Raman Crude Oil	88 %	0,5
Shorklu (2010)	5 %	0,1
This study	0 %	-

Table 4.4 –

Viscosity Reduction of Different Investigations Using Nano-sized Metal Catalysts

4.5 Experiment #2

Investigating the Catalytic Effect of Nano-sized Metals on Heavy Oil Upgrading during Microwave Heating.

Greff & Babadagli (2011) found that the presence of nano-sized first row transition metals could catalyze the upgrading of heavy oil when exposed to microwave radiation. The upgrading was found to lead to a substantial vaporization of lighter components, and a significant decrease in the viscosity of the liquids. This experiment aims to investigate the validity of their results, as they could have significant impact on the production and transporting of heavy oil. We are also applying some additional metals, to see how their performance compare to the ones previously investigated.

4.5.1 Experimental details

Samples

The samples were prepared in the same manner as in experiment #1, mixing 90 gram Athabasca bitumen with 10 gram n-dodecane.

Catalysts utilized

Nano-sized copper, iron, zinc, nickel and micron-sized copper was used. The catalysts were applied in concentrations of 0,1 wt% and 0,5 wt%.

Microwave Oven

For this experiment, a domestic Samsung ME-82 V-SS microwave oven was employed. It had a fixed radiation frequency at 2.45 GHz, and offered 7 power output levels ranging from 100 to 800 Watt. All the bottles containing samples during microwave treatment have the same dielectric properties.

Viscosity Measurement

A Brookfield LVDV-II+ Pro Viscometer was used to measure the viscosity of the samples before and after microwave treatment.

4.5.2 Procedure

1. 90 gram bitumen and 10 gram n-dodecane is mixed using a combined heater and magnetic steerer.
2. Nano-sized metal is added to the sample.
3. The sample is exposed to 30 minutes of ultrasonication.
4. The mass of the sample is measured.
5. The sample is placed at the center of the microwave oven.
6. Sample is heated at 300W for 30 minutes, contained by a lid to keep vaporizing gases from escaping.
7. Sample is removed from the microwave chamber and allowed to cool off.
8. After the sample has cooled off, the mass of the sample is measured.
9. Viscosity of each sample is measured at T = 21, 25, 35, 50, 65, 80, 100 ^{o}C.
10. The measured viscosities are fitted to a power law curve.

4.5.3 Results and Discussion

Table 4.3 presents the viscosity measurements for each sample.

Sample	Concentration of particles, wt%	Viscosity [cP]		
		25 ^{o}C	50 ^{o}C	100 ^{o}C
Base mix	0	5825	755,0	54,7
Base mix treated	0	8278	1020,0	76,5
Nano Iron	0,1	8318	1023,3	78,3
	1	14797	1283,5	95,4
Nano Nickel	0,1	8438	1092,9	80,4
	1	13689	1773,0	130,4
Nano Zinc	0,1	9778	1073,0	82,1
	1	15474	1698,1	129,9
Nano Copper	0,1	9568	1040,0	86,3
	1	16797	1840,0	151,5
Micron Copper	0,1	8678	1036,6	81,3
	1	15234	1745,0	142,7

Table 4.3 – Viscosity Measurements

The base case reveals that the microwave treatment increases the viscosity of the sample by up to 40%, without the presence of a catalyst. Upon measuring the mass of the sample, it is found that around 1,7% of the sample has vaporized. This is natural due to the open nature of the experiment, but it reveals a weakness in that lighter components created by the aquathermolysis reaction may evaporate, leading to a higher final viscosity. This was also observed by Greff et. al. (2011). In order to keep track of how evaporation affects our measurements, the mass of each sample was measured before and after the microwave treatment.

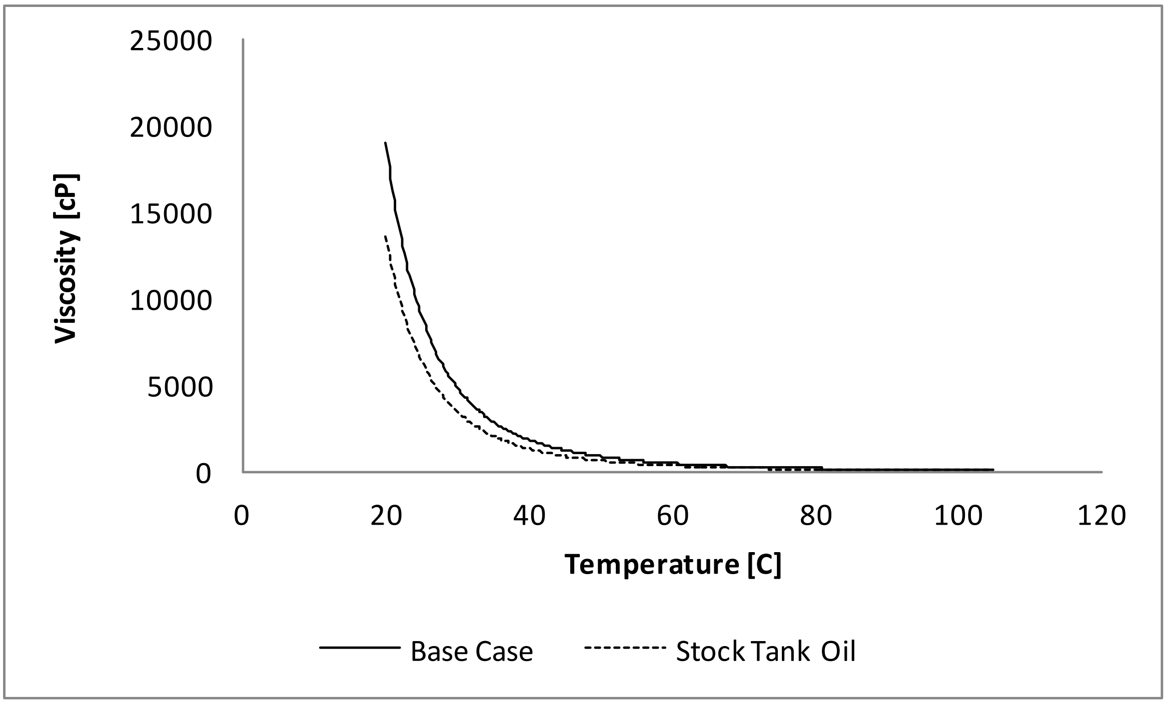

Figure 4.4 – Stock Tank Oil vs Microwave Base Case

Figure 4.5 and 4.6 show the power regression curves for nano-sized iron catalyst. These curves are based on the measurements for each sample, and are plotted together with the base case for reference.. With a 0,1 wt% concentration, the viscosity deviated very little from the base case. With a 1,0 wt% concentration however, a noticeable increase in viscosity is observed. The graphs for the other catalysts are included in Appendix B. It is apparent that a consistent behavior is observed between all the metals.

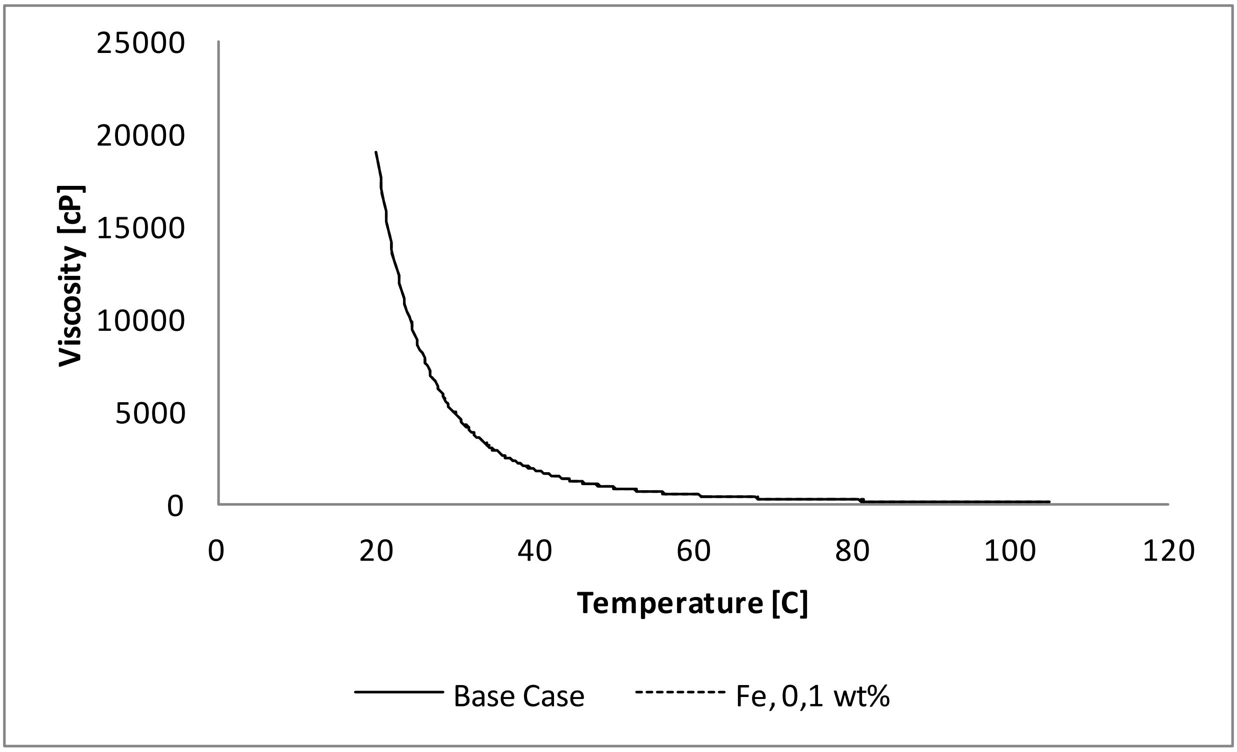

Figure 4.5 – Viscosity vs Temperature, 0,1 wt% Iron Catalyst

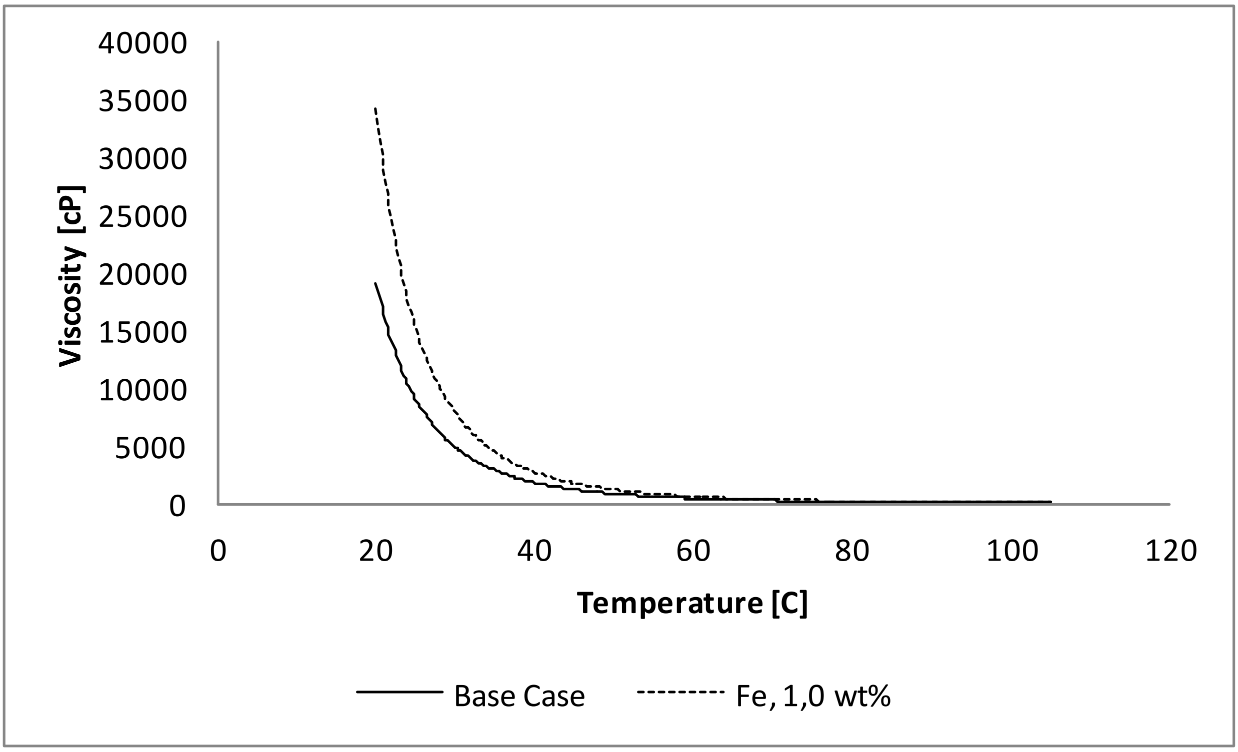

Figure 4.6 – Viscosity vs Temperature, 1,0 wt% Iron Catalyst

From table 4.3 it is observed that micron-sized copper is slightly less effective in increasing viscosity than nano-sized. This could be explained by the lower surface area, but the difference is small enough to be explained by statistical variance.

Figure 4.7 shows the relationship between vaporization, metal concentration and viscosity measured at 50 ^{o}C. We observe that a higher concentration of metal particles correlates with increased vaporization and higher viscosity. This has two primary explanations:

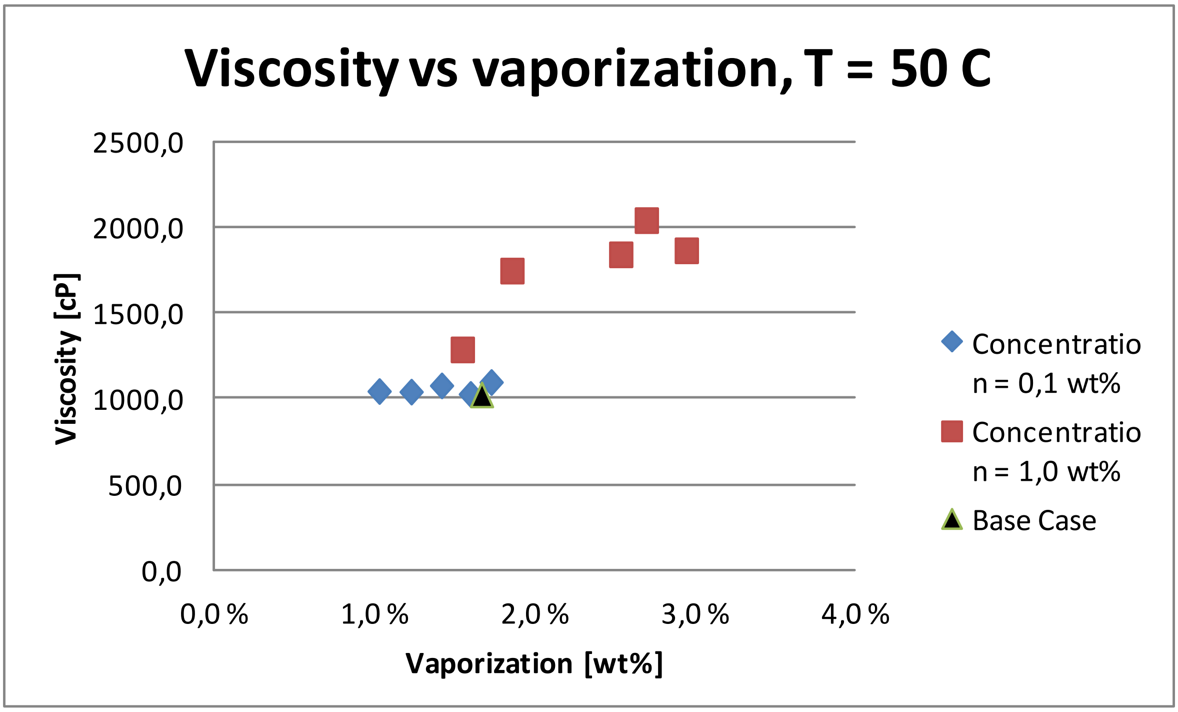

Figure 4.7 – Viscosity vs. vaporization

1) The increased concentration of metals increases the aquathermolytic reactions, creating lighter components that quickly evaporate due to the heat of the sample.
2) The increased metal concentration leads to a more rapid heating of the sample, resulting in a more aggressive evaporation.

Without a temperature sensor inside the microwave oven, it is hard to determine which of these is actually occurring. However, one observation indicates that the temperature may increase more rapidly when the metal concentration is higher. During the final experiment with 1,0 wt% copper, the sample caught fire inside the microwave. As this was never observed with lower concentration, it suggests that the increased vaporization may be caused by increased heating of the sample. The open nature of the experiment and lack of temperature sensor keeps us from concluding in one way or the other.

4.6 Conclusions

Nano-sized metals have been added to heavy oil for the purpose of decreasing the viscosity through catalytic aquathermolysis. Our results show that this has not been successful. Using nano-sized metals as the sole catalyst for wellsite upgrading of heavy oil is not deemed a feasible strategy.

Mixtures of nano-sized metals and heavy crude has been exposed to microwave radiation, for the purpose of upgrading the oil through aquathermolytic reaction. Our results indicate that this reaction may occur more effectively at high concentrations of metals. However, due to vaporization of lighter components, the resulting viscosity was higher than the initial. Nano-sized metals were found to increase the viscosity compared to micron-sized metals.

Further work is recommended to investigate the true nature of the vaporization:

- Heavy oil mixed with nano-metal catalysts should be exposed to microwave radition in a closed container, in order to preserve light components that may vaporize.
- The energy input and heating rate of the microwave should be compared to traditional heaters
- Nano-sized metals may have a catalytic effect in more traditional high-pressure, high-temperature upgrading processes. This should be investigated, as it may reduce the energy consumption and the amount of non-commercial byproducts.

5 Summary

Heavy oil makes up a very significant part of the world's discovered petroleum resources. While the world's production of heavy crude is increasing, many issues still keep the technological costs higher than for conventional oil. Advancements in extraction and production technology may have worldwide economic consequences.

Core-annular flow, while showing very promising results in laboratory tests, still has to overcome large unresolved issues before it may be applied as a generic industrial flow assurance technology. As the industry attention to solving these issues are currently limited, it is likely to remain a curiosity for special projects in the foreseeable future.

The effect of nano-sized metals on heavy oil viscosity has been investigated. It has not been found to significantly decrease the viscosity. Our results indicate that previous promising reports on this may have been wrongly interpreted. These catalysts are not judged have a future in surface processing on a commercial scale.

Microwave heating of heavy oil mixed with nano-sized metals was also investigated, for the purpose of catalyzing an upgrading effect referred to as aquathermolysis. Reduced viscosity was not achived, but it was discovered that increased metal concentration increases vaporization, which may be an effect of upgrading. Further studies are needed to conclude in this matter.

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Appendix A

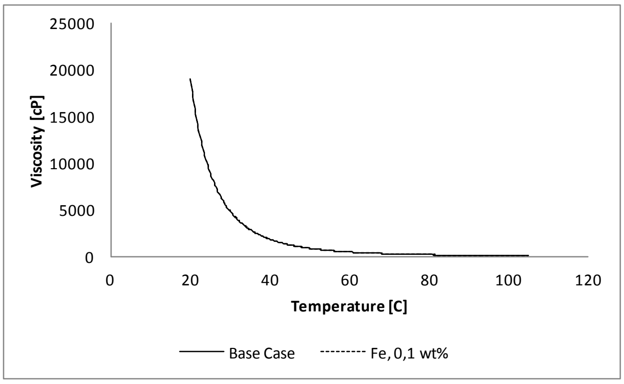
Tables & Graphs:

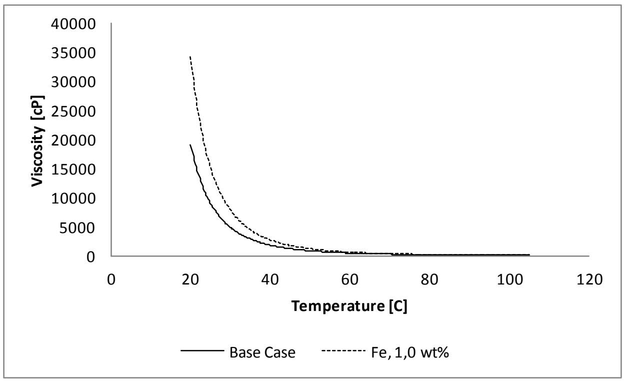
Repeatability Test			
	T = 25 °C	T = 50 °C	T = 100 °C
Test 1	5814	750	55,2
Test 2	5889	755	54,7
Test 3	5839	760	56,2
Test 4	5759	745	55,1
Average	5825	753	55
Average deviation	1,9 %	0,7 %	0,8 %

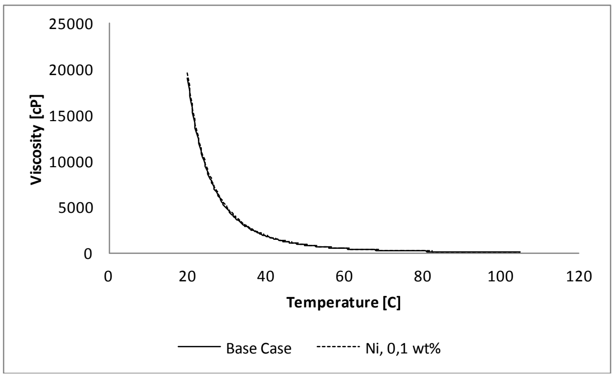
Table A-1 – Repeatability Test, Experiment #1

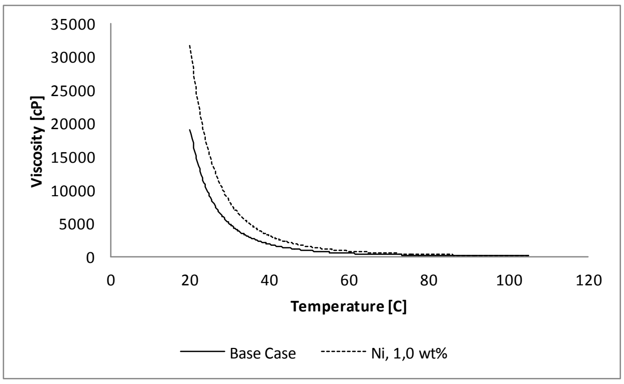
Appendix B

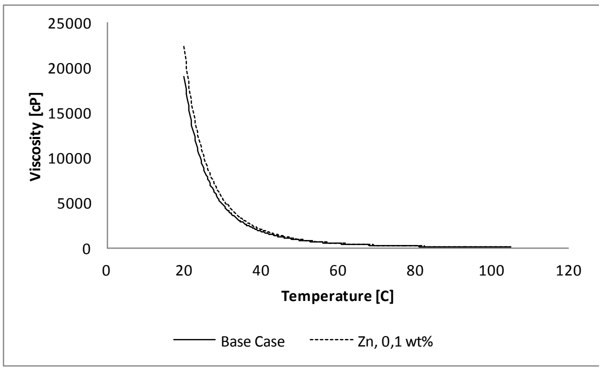
Viscosity plots from Experiment #2

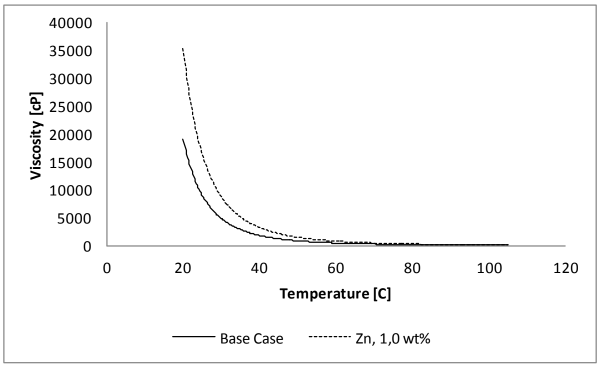


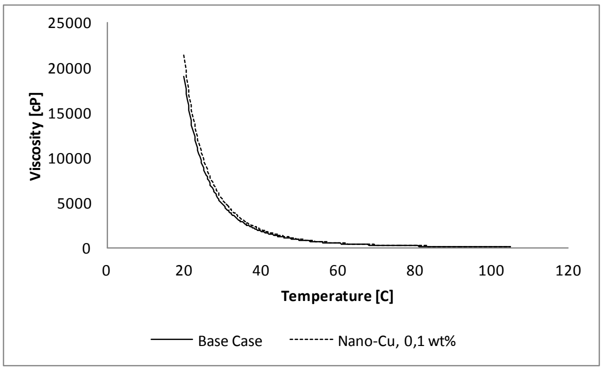


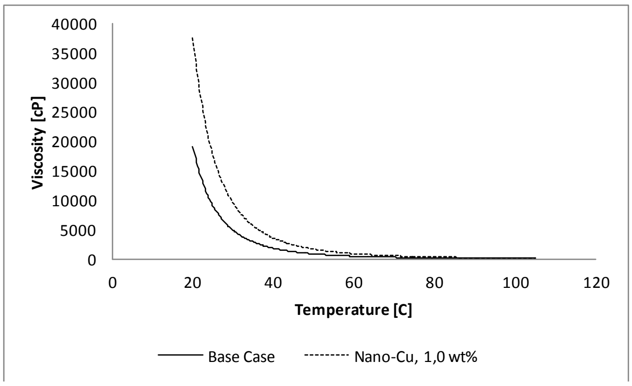


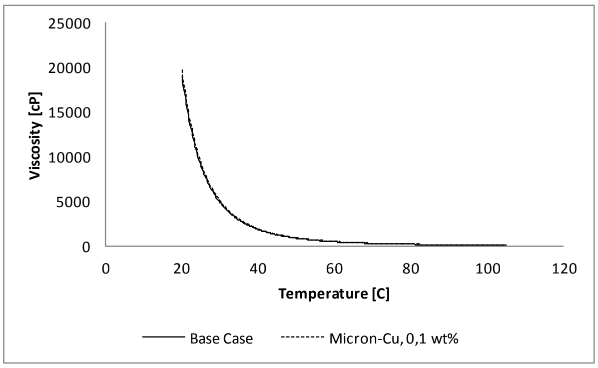


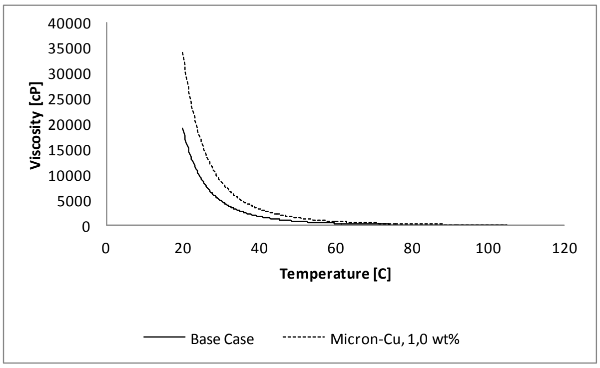


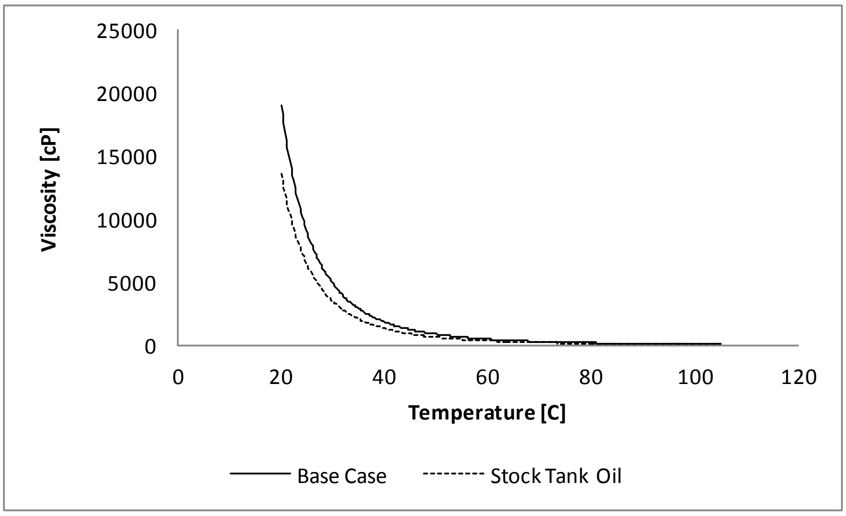






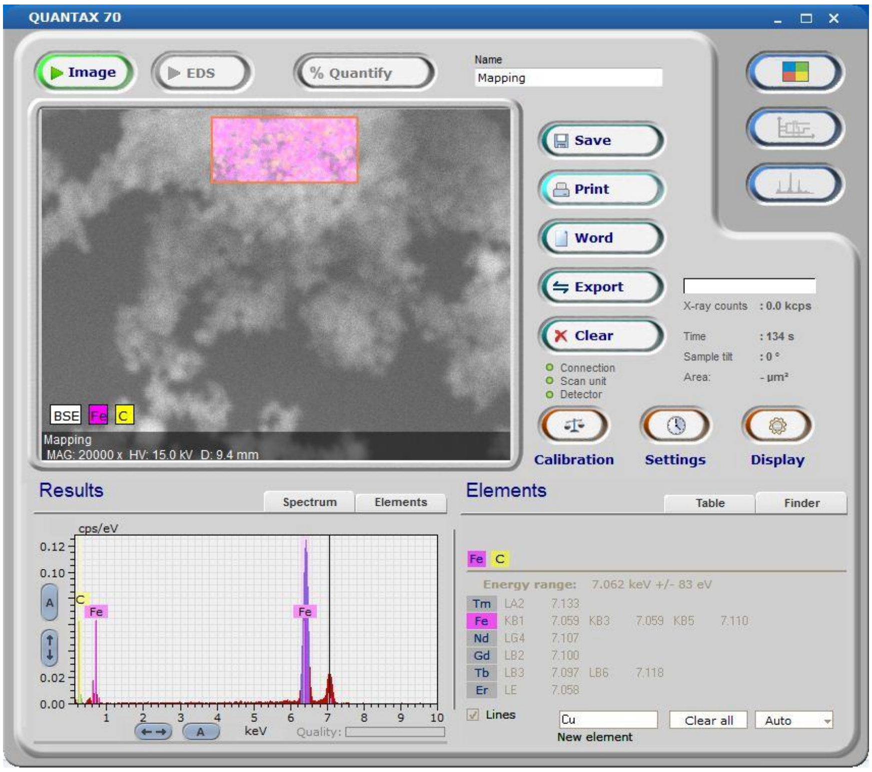

25000
20000
15000
10000
5000
0
Viscosity [cP]
0
20
40
60
80
100
120
Temperature [C]
Base Case
Micron-Cu, 0,1 wt%


40000
35000
30000
25000
20000
15000
10000
5000
0
Viscosity [cP]
0
20
40
60
80
100
120
Temperature [C]
Base Case
Micron-Cu, 1,0 wt%

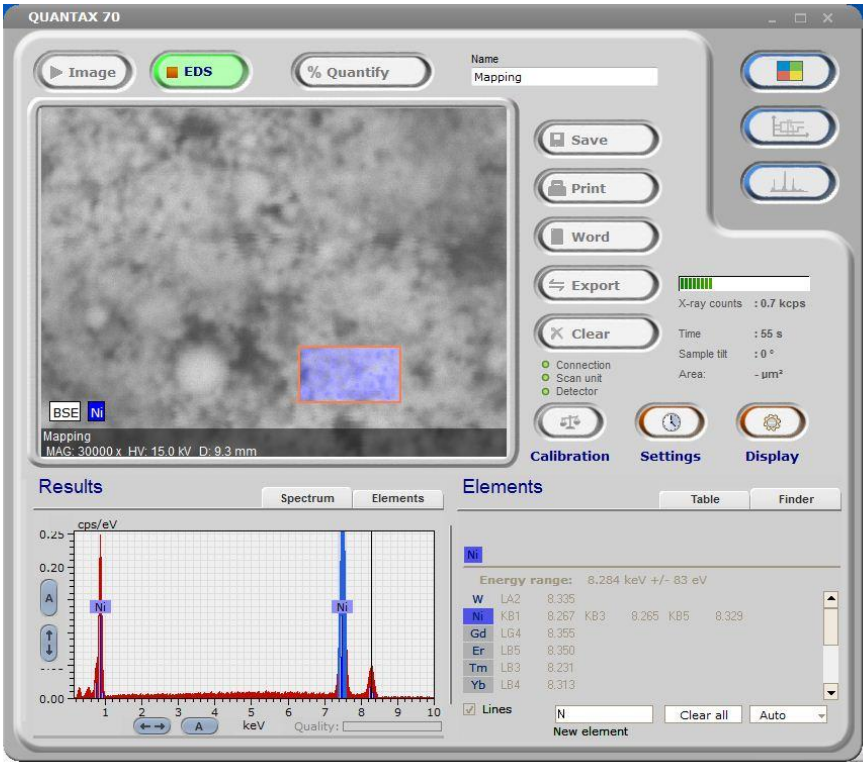

25000
20000
15000
10000
5000
0
Viscosity [cP]
0
20
40
60
80
100
120
Temperature [C]
Base Case
Stock Tank Oil

Appendix C

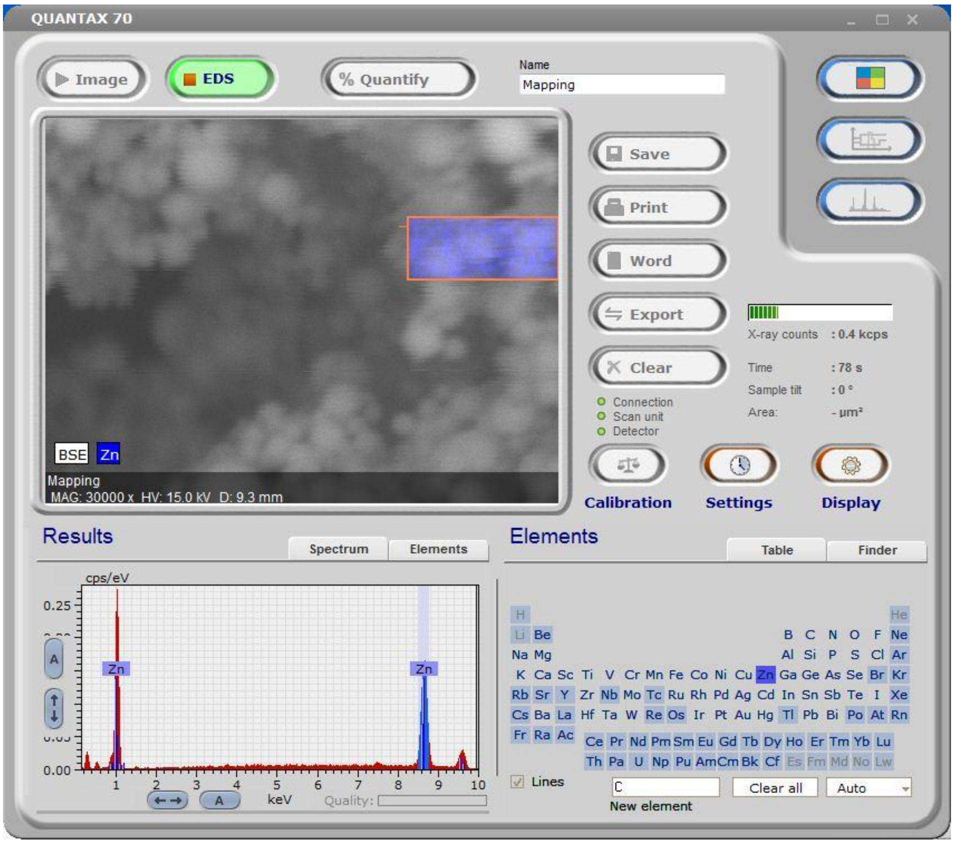
SEM Results



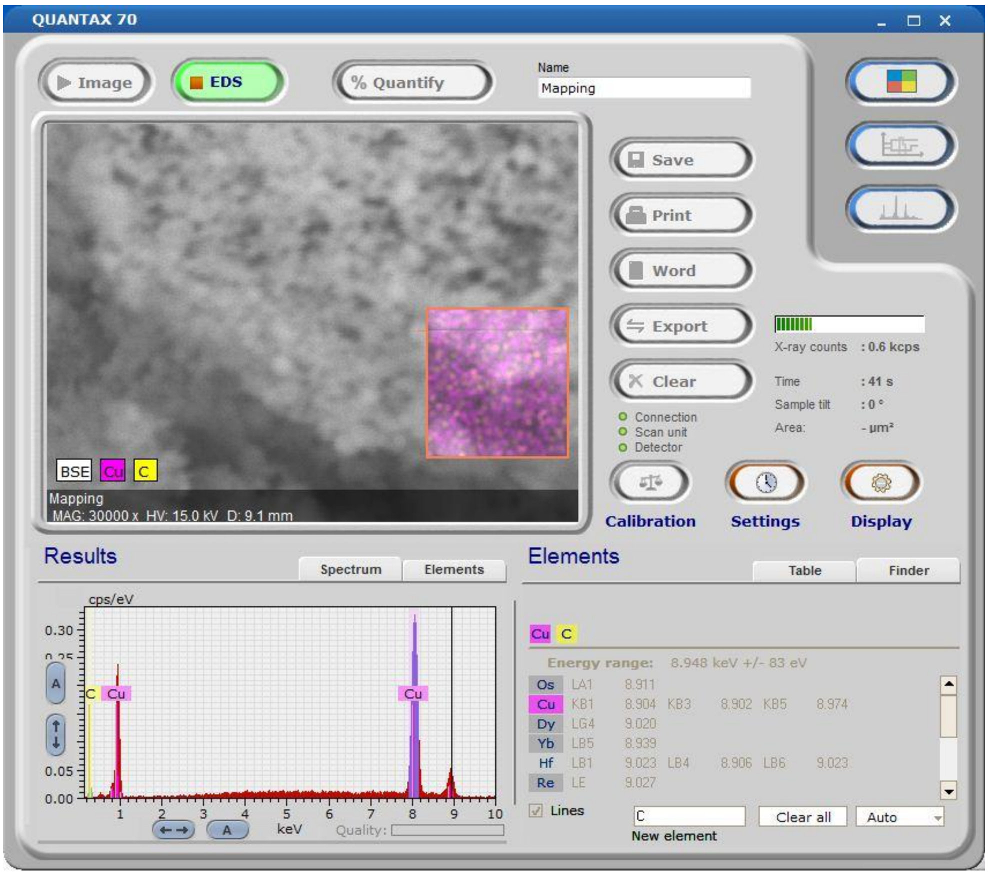
Iron – 40-60 nm



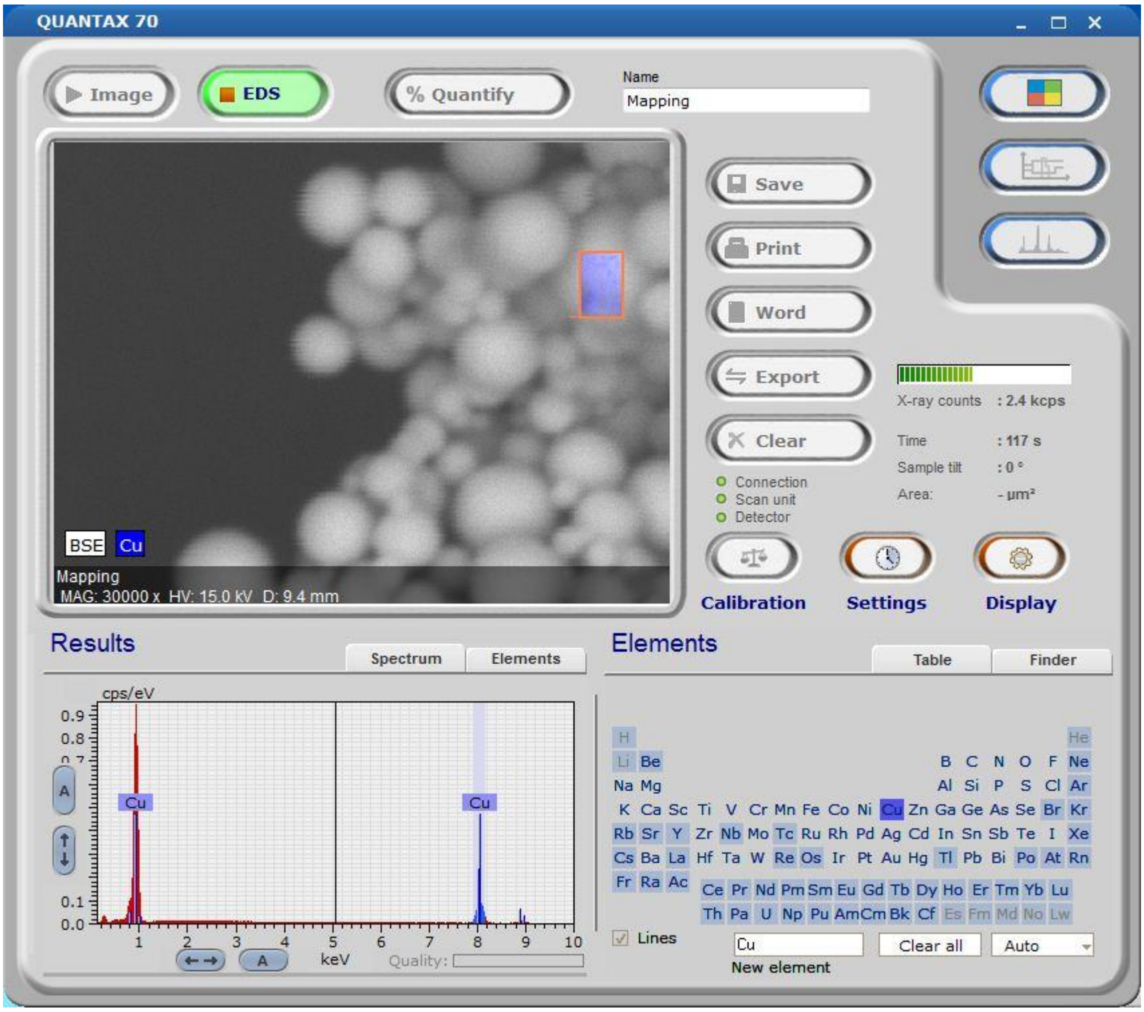
Nickel – 40-60 nm



Zinc – 40-60 nm



Copper – 40-60 nm



Copper – 500 nm

SI metric unit conversions

bar x 100,000	=	Pa
bbl X 0.158987	=	m^3
bbl/d x 1/543,440	=	m^3/s
cp x 0.001	=	$N\text{-}s/m^2$
F (F-32)/1.8	=	°C
ft x 0.3048	=	m
ft^3, cuf x 0.0283169	=	m^3
in x 0.0254	=	m
lb, lbm x 0.453593	=	kg
lb/ft^3, lbm/ft^3 x 16.0185	=	kg/m^3
psi, psia, psig x 6894.76	=	Pa
scf/STB x 0.17811	=	m^3/m^3