KE1

Development of a Commercial, Fully-Continuous, Supercritical Fluid Extraction Process for Oil Recovery from Waste

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ABSTRACT

This work is a case study on the development of a supercritical fluid extraction (SFE) process that began over twenty years ago as part of curiosity driven research and a desire to treat contaminated soils using supercritical fluids. Early work explored the measurement of fundamental thermodynamic and mass transfer properties. Commercialization was a faint long term hope but the relatively low value of the compounds found in contaminated soils (and many wastes), coupled with the typically large volumes, lead to the recognition that a batch or semi-batch SFE process was unlikely to be viable. This lead to the judgement that slurrying the soil was likely a necessary path to success. Research then focused on the impact of water on both thermodynamic and mass transfer behaviour. Ultimately, this drove the development and demonstration of the first, bench-scale, fully-continuous treatment process using slurries.

In parallel, an experimental program was studying the effectiveness of SFE for the treatment of upstream oil and gas industry waste. Timing and supportive industrial sponsors provided the opportunity to design, build, and demonstrate a pilot-scale, fully-continuous system for the treatment of multiple waste streams. The system has proved successful following many challenges and several years of work.

Tools to model system performance, explore scale-up design and assess economic and environmental impacts have also been developed and continue to be refined. The net result of the experimental and modelling success is a compelling case for commercial application of the technology for the recovery of hydrocarbons from at least one waste stream. The economics offers a net savings to the waste generator, while remaining profitable as a processing facility. Environmentally, the application leads to a net reduction in greenhouse gas emissions and converts valuable materials in waste streams to products.

INTRODUCTION

Supercritical fluid extraction (SFE) has been considered as a possible remediation technology for the treatment of oil contaminated waste streams (consisting of a mixture of oil, solids and some water). These waste streams are most often generated in high volumes and therefore batch and batch-like supercritical processing is economically impractical. The development of a fully-continuous SFE process was judged to be necessary for a commercially viable process for the recovery of oil from waste streams. Figure 1 illustrates a simplified process schematic. Supercritical carbon dioxide (SC CO_2) is used to extract oil from a waste stream in a counter-current high-pressure extractor. Fully-continuous operation is achieved by adding sufficient water to the waste stream so that it can be pumped into the extractor, easily flow down through the extractor and finally flow out of the bottom of the extractor. The water is recovered from the treated residuals and reused.

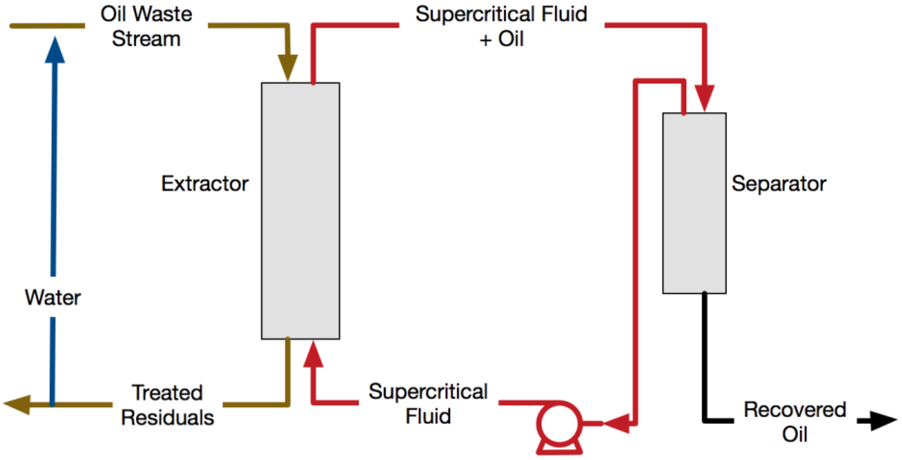

Figure 1. Simplified fully-continuous process schematic

This depiction of a commercial end-point was certainly not recognized at the outset of the overall research program. The desire for commercial implementation was present in the beginning but the form that this would take only became evident over time. This paper provides an overview of the development path and is structured somewhat chronologically. It starts with early foundational studies, proceeding to bench-scale application studies, on to pilot-scale studies and finally to commercialization work. However, the information presented is not fully chronological as foundational studies, bench-scale studies and pilot-scale studies continue to occur in support of the development of each of the larger scales.

FOUNDATIONAL STUDIES

Foundational studies of various forms have been undertaken from the beginning and continue to be an important part of the research and development effort. Examples of foundational studies include determination of partition coefficients, measurement of mass transfer coefficients, equilibrium studies and supporting modelling efforts.

These studies started with measurement of partition coefficients of polynuclear aromatic hydrocarbons (PAHs) and chlorinated aromatics between $SCCO_2$ and soil [1]. Partition coefficients define the thermodynamic limit for the supercritical fluid flow required for a given extraction task. The minimum supercritical fluid flow required is important in eventual scale-up as it drives the energy requirements and associated operating costs of the supercritical process. These partition coefficient studies were small scale and involved spiking dry soil with the compound(s) of interest. The results showed a dependence on the compound's properties, the experimental conditions and the soil's properties.

Mass transfer behaviour influences contact times required and how much supercritical fluid beyond the thermodynamic minimum may be required. Contact times ultimately control the extractor size required for a given processing capacity and this extractor size will drive a significant portion of the capital costs. Initial experiments quantified mass transfer coefficients in soils as a function of water content [2]. These experiments were conducted with a static bed of soil and used an on-line UV-Vis detector to detect the amount of contaminant extracted as a function of time. Increasing the water content of the soil from 5 wt% to 20 wt% lead to a decrease in the prevailing mass transfer coefficient by approximately a factor of 250. Subsequent experiments explored whether mixing could overcome the impact of the water on mass transfer [3]. The addition of mixing and baffles lead to mass transfer coefficients for soil with 200 wt% water approaching dry soil values (Figure 2).

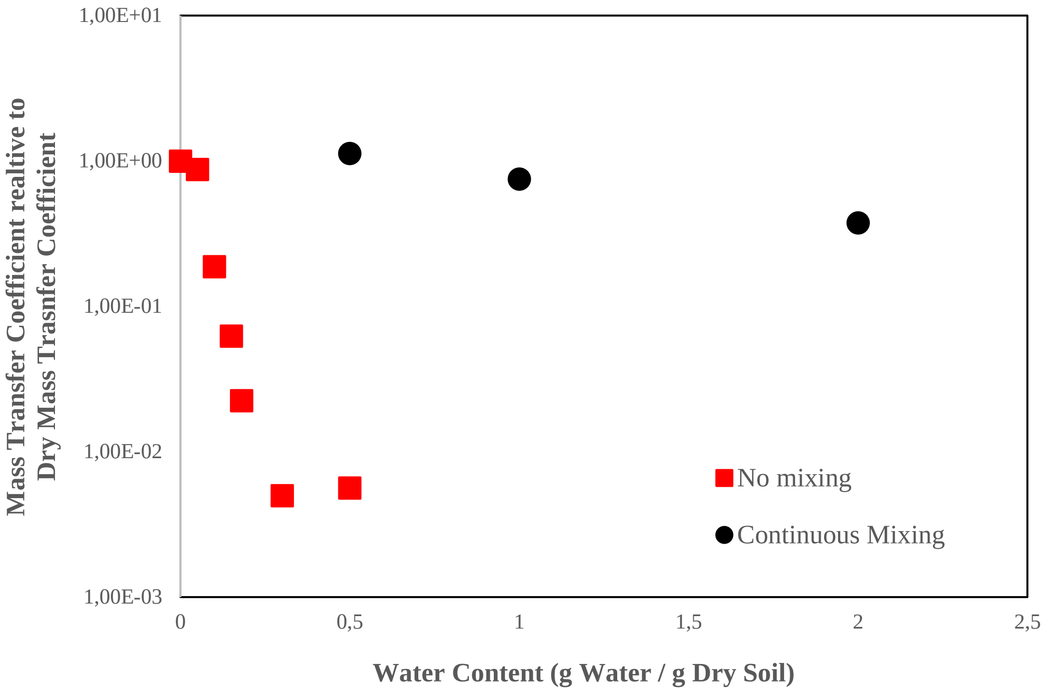

Figure 2. Mass transfer coefficients as a function of water content

Equilibrium studies continue today with the measurement of initial solubilities of complex mixtures [4]. Bitumen and heavy oils contain hundreds of components including a large number of compounds that are unidentified. The measurement of the initial solubility, akin to an initial boiling point for a complex mixture, as a function of conditions and modifier use, provides essential baseline data.

Modeling has been a component of the foundational studies. Models provide two functions: (i) support interpretation of experimental results and (ii) aid in the design and development of applications. Early design driven models explored minimizing energy cycle requirements (energy per mass of solute recovered) through the integration of thermodynamic properties (from Equations-of-State) and solubility correlations [5]. The results show that the lowest energy per mass conditions do not correspond to the operating conditions associated with maximum solubility. Modelling work continues with the further integration of mass transfer behaviour, multi-component and complex mixture capability, differing process configurations together with capital cost data to support assessment of different applications and different process designs.

BENCH-SCALE STUDIES

Many bench-scale studies were conducted during the development of the fully-continuous SFE process for the extraction of oil from waste streams. These bench-scale studies can be categorized into two groups: (i) bench-scale process studies which focused on the development of a fully-continuous SFE process and (ii) bench-scale application studies, which investigated the feasibility of SFE for the extraction of oil from different waste streams. These studies are briefly presented in the sections below.

Bench-scale process studies

The evidence that contaminants could be successfully extracted from slurries given sufficient mixing spurred the initial bench-scale fully-continuous system. Some key decisions were made in the pursuit of this first fully-continuous system:

1. It was decided to operate counter-currently to take advantage the well-established benefits of this configuration over a uniformly mixed vessel.
2. A method of passive mixing would be used to avoid the high cost anticipated with active mixing in larger units.
3. A high length to diameter ratio would be selected to avoid costly large diameter pressure vessels.

The first bench-scale fully-continuous system consisted of an extractor (50 cm in height, 4.2 cm inside diameter) with internal baffles to promote passive mixing (Figure 3). The system was controlled manually (adjusting flows on the CO_2 and slurry pumps) to achieve the desired pressure and a low level of slurry near the bottom of the extractor. A low level of slurry meant that the SC CO_2 was the continuous phase for the bulk of the extractor length which is desirable for good mass transfer. It took considerable time and experience to learn how to operate the system manually. The slurry level inside the vessel frequently dropped to zero, leading to SC CO_2 exiting the bottom of the vessel. Equally, the slurry level often increased to a point where it filled the vessel, leading to plugging in the SC CO_2 outlet line. Ultimately, a series of successful experiments were completed [6]. Subsequently, level control was added to the system, leading to a nearly ten-fold increase in the measured mass transfer coefficients [7].

Figure 3. First bench-scale fully-continuous system

Bench-scale application studies

Several studies were performed on a bench-scale batch SFE system to investigate the feasibility of SFE for the extraction of oil from different waste streams. Initial studies [8-11] focused on drilling waste as the waste stream. As seen in Figure 4, these studies showed that different types of oil (diesel oil or other drilling fluids such as Distillate 822 and HT40N) could be successfully extracted from different drilling wastes using SC CO_2 at moderate conditions of temperature and pressure, without the use of modifiers. However, entrainment of solids and associated plugging were problematic.

Figure 4. Extracted oil and clean solids after treating drilling waste with SC CO_2

Further studies [12] were therefore conducted on the bench-scale batch system with slurries of drilling waste. The aim of these studies was to investigate the effect of water on the extraction of oil from a drilling waste slurry and thus evaluate the feasibility of treating this stream as a slurry in a fully-continuous process. As with previous studies, the results indicated that oil could be successfully extracted despite the presence of large amounts of water.

Bench-scale batch studies have also been performed on oil sands and oil sands slurries [13-14]. Again, as seen in Figure 5, these studies showed that bitumen in the oil sands could be extracted from oil sands and oil sands slurries, with and without modifier, at moderate conditions of temperature and pressure. Addition of toluene as a modifier increased the amount of bitumen extracted.

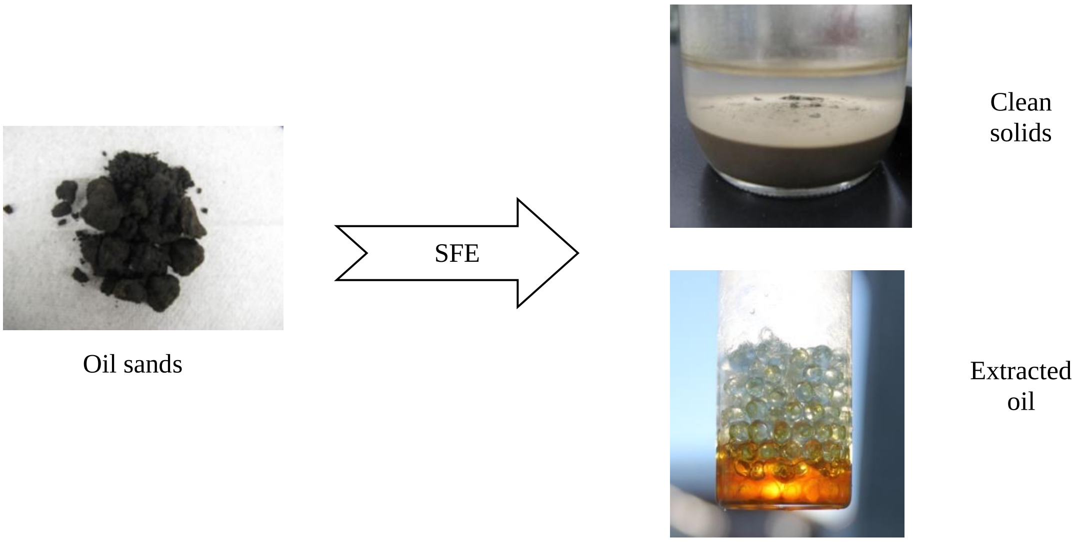

Figure 5. Extracted oil and clean solids after SFE treatment of oil sands

Bench-scale batch extractions of other process waste streams (i.e. mixtures of bitumen, other hydrocarbons, water and/or solids) are on-going. These dynamic extractions add a small quantity of bitumen or bitumen-containing waste stream to a mixed bench-scale batch extraction vessel. SC CO_2 (with or without modifier) flows through the vessel continuously and the extracted oil is collected as a function of time. Both the extracts and the material remaining in the extraction vessel at the end of the experiment are analysed [15]. The results show that the mass fraction of the bitumen that can be recovered is a function of T, P, and modifier concentration and that as much as 75 wt% can be recovered. As importantly, the compositional analysis shows that the recovered oil is lighter than the overall bitumen in the raw waste.

PILOT-SCALE STUDIES

The University of Alberta and the University of Guelph teams combined forces to develop a pilot-scale fully-continuous treatment unit for drilling waste. This effort combined the bench-scale success in treating contaminated solids using a fully-continuous SFE process with the bench-scale success in treating different oil contaminated waste streams in a batch system. Photos of the system are provided in Figure 6.

Figure 6. Pilot-scale fully-continuous system

Designing, building and commissioning of the pilot-scale fully-continuous SFE system took several years. During the design stage, the main challenge was that the desired process components were often too big, too small or too different to easily source. Adaptations and custom supply became common. Building at this scale within a university lab environment created challenges to prevailing norms and policies. Commissioning brought surprises that, in some cases, took far too long to resolve. Troubleshooting each element took time to work through and to build operator comfort. Ultimately, the system worked and effectively extracts oil from the waste stream.

System control is an essential element for the development and operation of the pilot-scale system. It is essential for both safety and operational performance reasons. Together with our industrial sponsor at the time, a Hazards and Operability Study (HAZOP) was completed to identify appropriate safety features and emergency shutdown protocols [16].

Designing the controllers was aided by a hydrodynamic model developed in Matlab/Simulink® [17-18]. Labview® was used to implement the controller design and to provide the user interface (Figure 7).

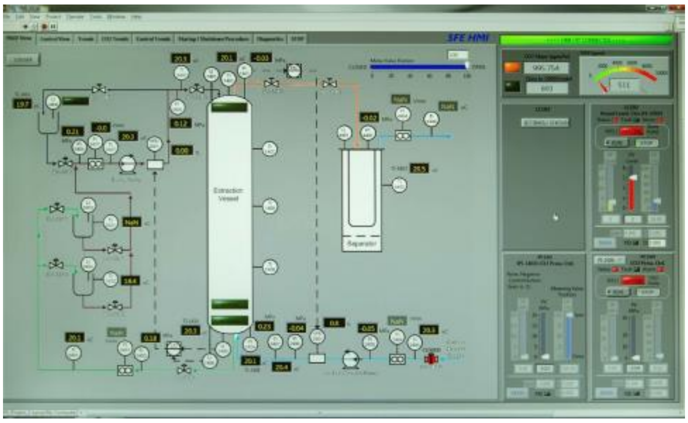

Figure 7. Labview® controller screen for the pilot-scale fully-continuous system

PROGRESS TOWARDS FULL COMMERCIALIZATION

The operational success of the pilot-scale system triggered pursuit of full commercialization. SCFCan Inc. was founded for the purposes of commercializing the technology for the drilling waste application. Business models and cases have been developed. They demonstrate the opportunity to decrease cost for the waste generator while providing an economic success story for the technology and an environmental win for society. The environmental wins include both the recovery of a resource that is too valuable to waste in addition to significant reduction in the life cycle greenhouse gas emissions. Although full commercialization is a goal that remains in the future, it does appear to be in the immediate future.

CONCLUSIONS

Reaching the current status of the fully-continuous SFE process required several key ingredients. First, talented students, staff and supporters were necessary. More than talented, these individuals had to be willing to try and be able achieve things that are different. Funding was also key throughout the process. The small initial research grants for new university professors are critical as they permit and seed essential work that slowly snowballs into technological success stories. Industry support, both financial and in-kind, permits building on early work. Industry and funding agency patience through stumbles is essential. Finally, the world of supercritical fluid processing requires exploration of thermodynamics, mass transfer, equipment design, process control, software development, process design, economics, environmental impact and more. Bringing together all of these key ingredients was necessary for development of the pilot-scale fully-continuous system and these elements will continue to be critical for the fully commercial process to be realized.

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