ISSN 0511-5728
The West Indian Journal of Engineering
Vol.37, No.1, July/August 2014, pp.44-49

The Extraction of Heavy Oil from Trinidad Tar Sands Using Supercritical Carbon Dioxide

David R. McGaw [a,Ψ], Sharad Maharaj[b], Aparna Parasram[c] and Warren Grayson [d]

[a,b,c] Department of Chemical Engineering, Faculty of Engineering, The University of the West Indies, St Augustine, Trinidad and Tobago; E-mails: drmcgaw@gmail.com; Sharad.Maharaj@sta.uwi.edu; aparasram@gmail.com

[d] John Hopkins University, Baltimore, USA; E-mail: wgrayson@jhmi.edu

[Ψ] - Corresponding Author

(Received 18 March 2014; Revised 27 May 2014; Accepted 30 June 2014)

Abstract: *The work described in this paper promotes the use of supercritical fluid extraction as an environmentally friendly alternative to the current hot water/steam process for the extraction of heavy oil from tar sand. An experimental programme was carried out on tar sand from the Parrylands district in South Trinidad, using a bench scale unit with supercritical carbon dioxide as the basic extraction fluid. In initially characterising the tar sand, Soxhlet extraction using toluene gave a bitumen content of 14.7% in the deposit and SARA (Saturate, Aromatic, Resin, Asphaltene) analysis showed the deposit to be mainly of resins, but with an asphaltene content of 12.6%. The experimental programme examined the effects of pressure 100 to 500bar, temperature 30 to 60ºC, particle size >20mm to <1mm, as well as the use of entrainers (pentane, hexane, heptane, and octane) to enhance recovery. The results showed the maximum extraction yield using carbon dioxide alone to be 4.5% by mass of the original charge in ~3hours, but this could be increased by at least another 1% by removing the charge and subjecting it to a second extraction. Pentane was the most effective entrainer, the yield increasing to 6.4% when using 45% pentane. Microscopic analysis showed the raw material to be a conglomerate mass initially, but breaking down to the individual sand particles with small amounts of oil cover after extraction. The final extracted sand could be subjected to bioremediation prior to charging back to the mine as an environmentally friendly disposal mechanism.*

Keywords: *Tar Sands, Supercritical Fluid Extraction, Carbon Dioxide, Entrainers, Environmentally Friendly Process*

1. Introduction

Tar sands are being increasingly exploited as an alternative hydrocarbon fuel resource, with the bulk of current production being from the deposits in the Athabasca area of Canada. In Trinidad fairly extensive deposits have been identified in the south of the country, the first evaluation being carried out by Rajpaulsingh and Kunar (1991), who estimated that there are around one billion barrels of tar/oil in place in 16 deposits. One third of this is from the Parrylands location covering an area of 330 hectares. In a follow-up study of the Parrylands deposit, involving analysis of borehole samples to 30 metres, Kuarsingh and Maharaj (1991) showed that the deposit would be amenable to surface mining and that the bitumen content is up to 15%. Bitumen gravity was measured to be 4.6^{o} API and viscosity 342 cp at 100˚C. The data indicated an oil sand of similar quality to Athabasca oil sand. Both ores can be also classed as high grade ores (with the Athabasca tar sands containing 14.4% bitumen), where any ore containing more than 10% weight bitumen, according to Carrigy (1967), can be classified as a high quality ore.

Such deposits may be exploited either by in-situ techniques or by surface mining, followed by appropriate subsequent processing to recover the heavy oil/bitumen: the choice mining technique is determined mainly by the depth, nature and extent of the deposit. Available in-situ techniques are of a thermal nature i.e., SAGD (Steam Assisted Gravity Drainage) or in-situ combustion; or alternatively by solvent extraction i.e., VAPEX. Use of these techniques, particularly in the Trinidad context, is described and discussed by Roopa and Dawe (2007). Similarly, external processing techniques can be of a thermal nature, e.g. steam treatment and pyrolysis, or by solvent extraction. The commercially established process, consisting of contacting mined sand with hot water/steam, as described by Houlihan (1984), suffers from the fact that it produces impounded tailings sludge, covering a vast area, thereby creating a significant environmental problem. Solvent extraction processes have shown promise - work by Cormack et al. (1977), Leung and Phillips (1985) and Ulrich et al. (1991) indicate high extraction efficiency at reasonable cost, albeit with the problems of solvent recovery, but with a reduction of the environmental problems which result from the hot water process.

Because of the negative issues associated with the established processes, enumerated above, more recent research for both in-situ and external processing has been directed towards the use of gaseous solvents. The obvious solvent to utilise in Trinidad would be carbon dioxide as it is readily available from the Ammonia Plants in Trinidad. Thus Roopa and Dawe (2010) have carried out a study of the potential for utilising carbon dioxide in a VAPEX type process for in-situ recovery at around its critical point by investigating the transfer characteristics of heavy oil into carbon dioxide. They concluded that reservoirs deeper than 1,500m were well suited to this type of process. However the tar sands in the Parrylands deposit in Trinidad are mainly at depths down to 30m, as reported by Kuarsingh and Maharaj, (1991). They are thereby more suited to surface mining and external processing. An alternative to the traditional hot water extraction process with much reduced environmental consequences could be the use of Supercritical Extraction (SFE).

Research has been reported using supercritical propane, notably by Eisenbach et al. (1983) and Subramanian et al (1995). In their work on Athabasca Tar sand, Eisenbach et al. (1983) used propane at 110^{o}C and 200bar pressure giving a total extraction of just over 9% (~ 60% of the oil in place). In their more comprehensive study of the tar sands of the Uinta Basin in Utah, Subramanian et al. (1995) covered four separate deposits operating at three different temperatures and pressures over the ranges 66^{o}C to 150^{o}C and 56bar to 173bar, with a maximum yield of 45% of the bitumen content of the tar sands. Roopa and Dawe (2010) demonstrated the use of carbon dioxide in 3 experiments carried out at around the critical point, but there are no reported comprehensive studies on the use of carbon dioxide under supercritical conditions where the extraction yields would be higher.

The work described in this paper investigates the use of supercritical carbon dioxide for extracting the heavy oil from tar sands over a wide range of operating conditions, and aims at evaluating the potential for using SFE in the extraction of the heavy oil from the tar sands located in the Parrylands district of Trinidad. The carbon dioxide would be recycled in the process, and there are no liquid effluents, so the process can be deemed to be environmentally friendly.

In order to develop data to evaluate the potential for the use of SFE using supercritical carbon dioxide as an extracting agent, the work programme covered the following:

1) Characterisation of the raw material in terms of quantifying the bitumen content of the indigenous tar sand and also in terms of the general composition of the bitumen.
2) Laboratory scale SFE experiments using carbon dioxide: This included the use of entrainers, to demonstrate the process and to identify the best operating conditions.
3) Investigating the changing structure of the tar sand mass during extraction using microscopy, to help characterise the waste product for waste disposal.
4) Characterisation of the extract using Gas Chromatography.

2. Materials and Methods

The raw material was supplied from the Parrylands site by the national petroleum company, Petrotrin. The experimental work was carried out in four stages, as follows:

Stage 1 – Characterisation of Deposit

There were two aspects to this stage, these being:

(i) Standard Soxhlet Extraction using toluene in order to measure the total hydrocarbons present in the deposit.
(ii) SARA (Saturate, Aromatic, Resin, Asphaltene) analysis on the extract from toluene distillation, to give a rough classification of the bitumen in terms of the normally quoted broad chemical groupings used by the petroleum industry for characterising heavy oils.

Stage 2 – Supercritical Fluid Extraction Experiments

The main part of the experimental programme was carried out with an Applied Separations Speed laboratory model Supercritical Fluid Extraction Unit using carbon dioxide as the extraction fluid. A 100ml extraction vessel was used throughout the experimental programme, the variables investigated were:

Pressure: 100 to 500bar (45^{o}C, 2.5mm particle size)
Temperature: 30 to 60^{o}C (250bar, 2.5mm particle size)
Particle size: >20 to <1mm (250bar, 45^{o}C)
Entrainer: pentane, hexane, heptane, octane (250bar, 45^{o}C, 3.8mm particle size)

The figures in the brackets above give the fixed values of the other conditions. All experiments were carried out in duplicate.

Stage 3 – Microscopic Analysis of the Tar Sand charged to the vessel, and also of the sand after extraction.

Both the sand charged to the vessel and the sand after extraction were analysed. Samples were transferred to glass slides and observed under an OLYMPUS BX 50 Light Microscope. Several pictures of the material were taken with a Pixera Penguin 5.8 MP digital, colour camera that was attached to the microscope.

Stage 4 – Product Analysis

The analysis was carried out using a Hewlett-Packard Model 5890 Series II Gas Chromatograph with Flame-Ionisation Detector (FID). An initial oven temperature of 35ºC was used and the temperature was ramped up at 5ºC /min to a final oven temperature of 300ºC and maintained at that value for 15 minutes. A fused silica capillary column (5m x 0.53 mm internal diameter; 0.1 µm film thickness) from Supelco was used in the process. Particle size analysis at the different stages of the process was carried out by sieve analysis.

3. Results and Discussion

3.1 Characterisation of Tar Sand Deposit

Soxhlet extraction using toluene gave a mean total bitumen extraction of 14.7% (3 samples). This is consistent with the results on the same deposit as reported by Kuarsingh and Maharaj (1991). SARA analysis of the extracted oil from Soxhlet is shown in Table 1 (2 samples).

Table 1. SARA results for oil extracted from Parrylands tar sand compared to that quoted for Athabasca tar sand according to Rahimi and Gentzis, (2006) and for Whiterocks tar sand as reported by Subramanian et al. (1995)

Component	Parrylands Tar sand	Athabasca Tar sand	Whiterocks Tar sand
Saturates (wt%)	21.9	17.3	35.7
Aromatics (wt%)	7.3	39.7	7.0
Resin (wt%)	58.2	25.8	54.5
Asphaltenes (wt%)	12.6	17.3	2.9

The SARA analysis had not previously been determined for this deposit, but had different characteristics to that reported for Athabasca deposits as shown in Table 1. It was similar however to that reported for the Whiterocks oil sand from the UINTA Basin deposit as reported by Subramanian et al (1995).

3.2 Supercritical Fluid Extraction Results

A typical extraction curve is shown in Figure 1, where the yield of oil as a percentage of the total mass charged to the reactor is plotted against extraction time. Figure 1 shows that the bulk of the extraction takes place in the first two hours, with extraction being essentially completed after three hours. Yields were calculated from initial charge and extract weight measurements, with the calculated yield estimated to be accurate to +/- 0.1%.

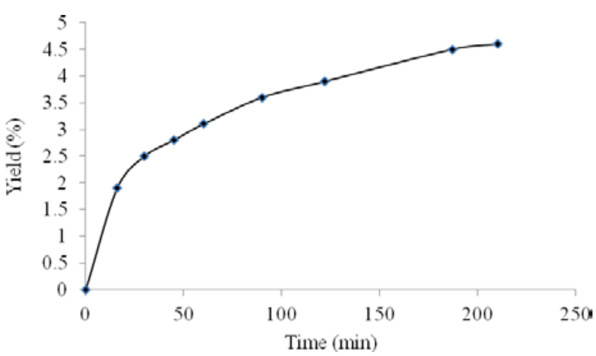


Figure 1. Typical extraction curve at 45°C and 250 bar

The final yields from the experiments where the pressure was varied are shown in Figure 2, where it is seen that the final yield increases steadily with pressure over the range 100 to 300 bar above which the yield was fairly constant with increasing pressure, at ~ 4.0% of the original mass of tar sand. The final yields from the experiments where the temperature was varied are shown in Figure 3. There appears to be a maximum yield at ~4.5%, when operating at 45°C.

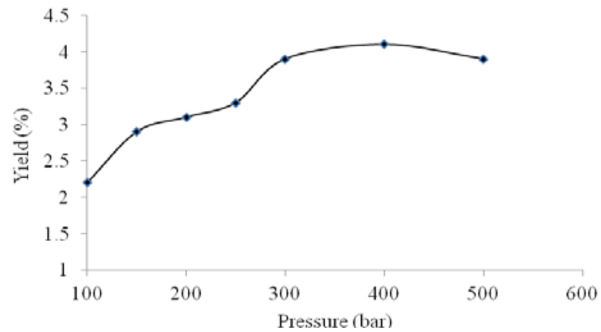


Figure 2. Effect of varying Pressure on Yield at a constant Temperature of 35°C

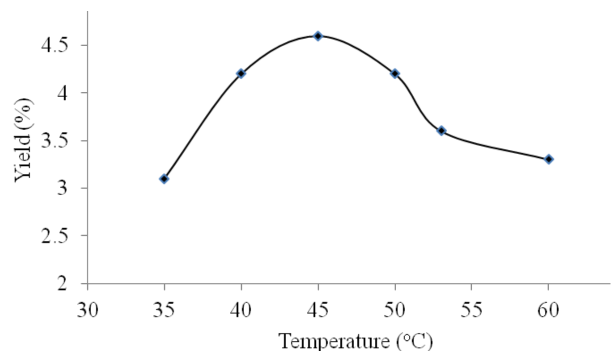


Figure 3. Effect of Temperature on Yield at a Constant Pressure of 250 bar

Initial particle size is an important variable as shown in Table 2. However, size reduction to <1mm is difficult due to the nature of the tar sand, such that ~2.5mm was deemed to be the lowest practical size. The use of alkane entrainers was found to increase yields, with pentane giving the best result as shown in Table 3.

Table 2. Effect of Particle size on Extraction Yield

Particle Size (mm)	Yield (%)
>20mm	2.17
~10mm	3.53
~5mm	4.05
~2.5mm	4.50
<1mm	5.10

Table 3: Effect of Entrainers on Yield

Entrainers	Yield (%)
30% Pentane	5.46
30% Hexane	5.20
30% Heptane	4.94
30% Octane	4.59
30% Pentane	5.46
30% Hexane	5.20

In a further series of experiments investigating the effect of the quantum of pentane addition on yield, the yield maximised at 6.4% using 45% of pentane as entrainer, as shown in Figure 4

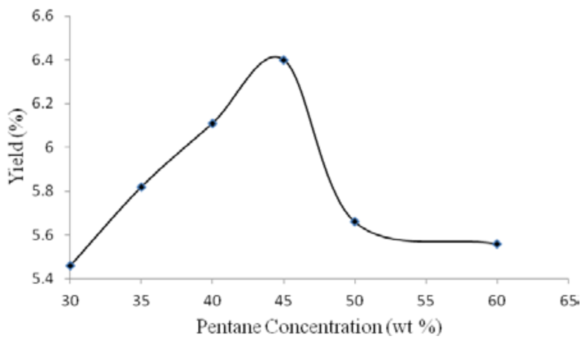
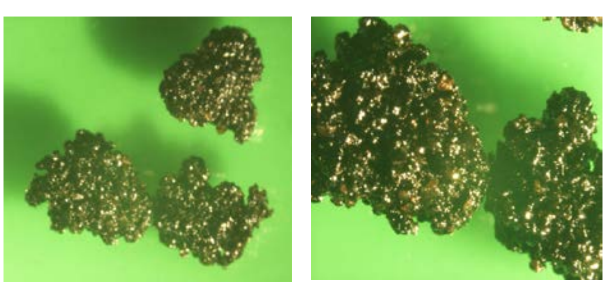


Figure 4. Effect of different concentrations of Pentane on Yield

The experimental results showed that it is possible to extract heavy oil from the Parrylands tar sands, the maximum yield from a simple extraction with carbon dioxide being ~4.5%, with the best operating conditions being 250 to 300 bar pressure and 45°C. The rates of extraction from this experimental programme were slightly less than those of Subramanian et al (1995), who used propane, but were similar when pentane was used as an entrainer. The experiments' varying particle size indicate that the tar sand charge to the extractor should be as small as is practical - size reduction being extremely difficult, due to the physical nature of the tar sand.

3.3 Evaluation of the Change in Physical Characteristics of the Tar Sands during Extraction

Photographs of typical particles prior to extraction and after extraction are shown in Plates 1 to 3. Plate 1 shows typical particles prior to charging to the extraction vessel indicating a conglomerate mixed mass of bitumen and sand particles of particle size 4 to 5mm as shown. Plate 2 is of particles after CO_2 extraction, showing separate sand particles, but still with some residual bitumen on the surface of individual particles.



(a) MAG 12.5 (b) MAG 20

Plate 1. Tar sand particles before supercritical extraction

Plate 3 is of particles after extraction with CO_2 utilising pentane as entrainer; these being rather cleaner than those in Plate 2, because of the higher extraction. The average size of the sand particles as shown in Plates 2 and 3 was ~0.4mm. The particles were still sticky, but broke up easily to the touch.

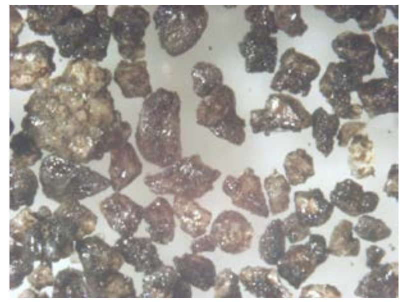


Plate 2. Tar sand particles after extraction with supercritical CO_2 only, MAG 10

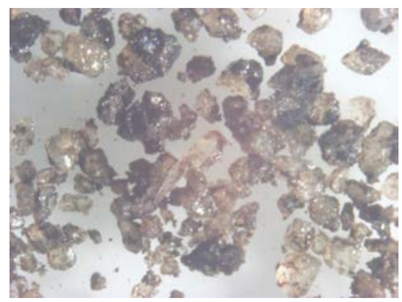


Plate 3. Tar sand particles after extraction with supercritical CO_2 and Pentane, MAG 10

Because the extraction was incomplete, an experiment was carried out on the residue particles from CO_2 extraction whereby they were broken up into a mass of individual particles and charged back into the extraction vessel, where a second extraction was carried out. A further 1% extraction was recorded, demonstrating that a two stage process was feasible.

3.4 Product Analysis

The extract was a thick, clear oil with a light brown colour. A typical chromatogram is shown in Figure 5, where it is seen that there are a large number of components in the range from C20 to C90.

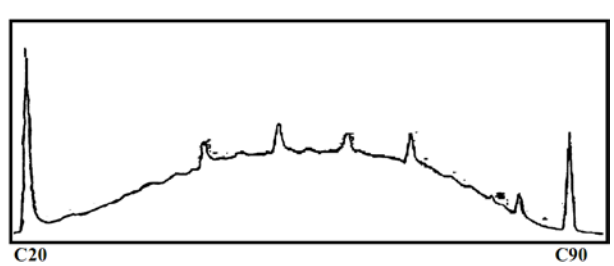


Figure 5. Chromatogram of Extracted Heavy Oil

The chromatogram was obtained from an analysis of the extract obtained at 250bar pressure and 45ºC. Extracts from other operating conditions gave similar chromatograms.

On the basis of the GC results, the oil obtained can be classified as a heavy crude oil which can be processed in refinery configurations suitable to heavy oils. The saleable cuts produced from fractional distillation of an oil of this type are used as diesel oil, lubricating oil, waxes, polishes, fuel oil for ships as well as central heating and bitumen for road paving and roofing(The Oil Drum 2006).

4. Implications of Results

The work has shown that the bitumen from the Parrylands tar sands deposit can be extracted by SFE using carbon dioxide to produce a clear, heavy oil. Notwithstanding the fact that much of the heavy oil is separated from the sands, as shown in Plates 2 and 3, there is a need to determine how the bulk of the remaining oil can be extracted. Two approaches have been tried with some success:

1) Use of an entrainer, pentane being the most suitable of those investigated in this work. As the carbon number of the alkane increases, it gets heavier and may easily diffuse within the oil sand matrix. From pentane to octane, the higher carbon number solvents have smaller diffusion co-efficients, which according to Funk (1979), would have led to poor mass transfer and resulted in lower extraction yields.
2) Utilisation of a two stage (or multistage) process whereby the extracted solid mass from the first stage is broken down to individual particles and subjected to a second carbon dioxide extraction. Possible consideration could however be given to another potential supercritical solvent, since the use of supercritical carbon dioxide in a single experiment only increased the extraction from 4.5% to 5.5% of the initial charge, equivalent to ~40% of the oil in place.

The overall system would entail: (i) Mining of Tar Sand, (ii) Transportation to a Processing Site, (iii) Processing, (iv) Transportation of Spent Sand back to Mine Site, (v) Charging of Spent Sand back into Mined Out Areas, and (vi) Rehabilitation of Mine Area e.g., into Agriculture. The extracted heavy oil would be transported to the refinery for processing.

The use of SFE would be a better process than the current water/steam extraction in environmental terms in that there are no slurry tailings. The spent sand which will have a small amount of oil still attached to it can be subjected to standard bioremediation techniques, either prior to charging back into the mine location, or after putting back into the mine.

Further work should focus on (1) and (2) approaches above towards optimising the process. Successful optimisation may stem from considering another, more effective, supercritical solvent with pentane as a co-solvent. A potential supercritical solvent could be propane, which has an excellent extracting capability and tends to produce a de-asphalted oil, thereby reducing processability problems during refinery processing(Subramanian et al 1995).

5. Conclusions

Several conclusions can be drawn, including:

1) The bitumen content of the oil sand deposit at Parrylands is 14.7%. This falls into the category of a rich grade tar sand, making the reserve at Parrylands a high-quality ore.
2) SARA analysis shows that the oil at Parrylands contains 21.9% saturates, 7.3% aromatics, 58.2% resins and 12.6% asphaltenes.
3) Clear heavy oil can be extracted using supercritical fluid extraction with CO_2.
4) The optimum process conditions for supercritical extraction with CO_2 were 45^oC and 250 bars, giving an extract of 4.5% of the original mass of tar sand in about 3 ½ hours.
5) The use of entrainers generally gives an increase in the extraction yield and shortens the extraction time.
6) The highest oil yield was 6.4% and was obtained by using 45% pentane. However, an increase in entrainer carbon number showed a decrease in oil yield.
7) The microscope work clearly showed there was a break up of the conglomerate mass of the initial charge during extraction to release the individual sand particles. These individual sand particles however still had a small amount of bitumen on the surface showing incomplete extraction. There was less residual bitumen on the particles when pentane was used as an entrainer.
8) The GC results showed supercritical CO_2 extract components to be in the range C20 to C90, and
9) The work demonstrates that the use of Supercritical Fluid Extraction to extract the heavy oil from tar sands shows good promise as an environmentally friendly process, whereby the tar sand could be mined then processed after which the clean residue could be charged back into the mined out area.

References:

Rajpaulsingh, W. and Kunar, L. (1991), "An evaluation of the mineable tar sands, Trinidad West Indies", in: Meyer, R.F. (Ed), *Heavy Crude and Tar Sands: Hydrocarbons for the 21st Century: 5th UNITAR International Conference on Heavy Crude and Tar Sands*, Petroleos de Venezuela, Vol.1, pp. 437-442.

Kuarsingh, H. and Maharaj, U. (1991), "Exploitation prospects for outcrop deposits in Southern Trinidad," in: Meyer, R.F. (Ed), *Heavy Crude and Tar Sands: Hydrocarbons for the 21st Century: 5th UNITAR International Conference on Heavy Crude and Tar Sands*, Petroleos de Venezuela, Vol.1, pp. 141-154.

Carrigy, M.A. (1967), "The physical and chemical nature of a typical tar sand: Bulk properties and behaviour", in: Barrows, G.H. (Ed.), *7th World Petroleum Congress: A Special Report*, World Petroleum Congress, pp. 573-581.

Roopa, I. and Dawe, R.A. (2007), "Gravity-assisted drainage techniques for heavy oil recovery in Trinidad: A review of macroscopic processes and film drainage considerations", *West Indian Journal of Engineering*, Vol.29, No.2, pp.50-64

Houlihan, R. (1984), "An overview of oil sands extraction-commercial technology and new techniques", in: Meyer, R.F., Wynn, J.C. and Olson, J.C. (Eds.), *The Future of Heavy Crudes and Tar Sands*, McGraw-Hill Inc., pp. 1076-1086

Cormack, D.E., Kenchington, J.M., Phillips, C.R., and Leblanc, P.J. (1977), "Parameters and mechanisms in the solvent extraction of mined Athabasca oil sand", *The Canadian Journal of Chemical Engineering*, Vol.55, No.10, pp.572-580.

Leung, H. and Phillips, C.R. (1985), "Solvent extraction of mined Athabasca oil sands", *Industrial and Engineering Chemistry Fundamentals*, Vol. 24, No.3, pp.373-378.

Ulrich, R.K., Koppaiah, M.K. and Majumdar, V.K. (1991), "Application of the rotating disc method to the study of bitumen dissolution into organic solvents," *The Canadian Journal of Chemical Engineering*, Vol.69, No.8, pp.825-832.

Eisenbach, W.O., Niemann, K. and Gottsch, P.J. (1983), "Supercritical fluid extraction of oil sands and residues from oil and coal hydrogenation", in: Paulaitis, M.E. (Ed.), *Chemical Engineering at Supercritical Fluid Conditions*, Ann Arbour Science, pp. 419-443.

Subramanian, M., Deo, M.D. and Hanson, F.V. (1995), "Supercritical fluid extraction of UINTA basin bitumens", in: Meyer, R.F. (Ed.), *Heavy Crude and Tar Sands: Fuelling for a Clean and Safe Environment: 6th UNITAR International Conference on Heavy Crude and Tar Sands*, United States Department of Energy, Vol. 2, pp.193-204.

Roopa, I. and Dawe, R.A. (2010), "A laboratory study of recovery with carbon dioxide around critical conditions of Trinidad's heavy oil and tar Sands", *Petroleum Science and Technology*, Vol.28, pp.1544-1554.

Rahimi, P.M. and Gentzis, T. (2006), "The chemistry of bitumen and heavy oil processing", in: Hsu, C.S. and Robinson, P.R. (Eds.), *Practical Advances in Petroleum Processing*, Springer New York, pp.150-154.

The Oil Drum (2006), "Getting gas from crude", Accessed March 12th 2014, from http://www.theoildrum.com/story/2006/3/13/11938/9181

Funk, E.W. (1979), "Behaviour of tar sand bitumen with paraffinic solvents and its applications to separations for Athabasca tar sands", *The Canadian Journal of Chemical Engineering*, The Canadian Society for Chemical Engineering, Vol.57, pp.333-341.

Authors' Biographical Notes:

David R. McGaw *is Professor Emeritus at The University of the West Indies, Chemical Engineering Department, where he continues to advise on a number of research projects. Prof. McGaw holds B.Sc. and M.Sc. degrees in Chemical Engineering (Wales) and a Ph.D. degree in Chemical Engineering from The University of the West Indies, Trinidad. He is also a Fellow of the Institution of Chemical Engineers (FIChemE).*

Sharad Maharaj *is Instructor III at The University of the West Indies, Chemical Engineering Department. Dr. Maharaj received his B.Sc. degree in Chemical and Process Engineering and Ph.D. degree in Chemical Engineering from The University of the West Indies, Trinidad.*

Aparna Parasram, *is currently employed with the Petroleum Company of Trinidad and Tobago. Mrs. Parasram received her B.Sc. degree in Chemical and Process Engineering and M.Sc. degree in Petroleum Engineering (with distinction) from The University of the West Indies, Trinidad.*

Warren Grayson *is Assistant Professor at Johns Hopkins University, Biomedical Engineering Department. Prof. Grayson received his B.Sc. degree in Chemical and Process Engineering from The University of the West Indies, Trinidad and his Ph.D. degree in Biomedical Engineering from Florida State University.*

■