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Analysis of Partially Dried, Solvent Extracted Oil Sands Samples for Naphtha and Water

by

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Introduction

A series of drying tests have been carried out at UBC in order to determine the drying curve for the devolatilisation of solvent extracted, oil sands agglomerates. The tests were carried out in a small fluid bed reactor at about 200°C. Samples of agglomerates were provided by NRC; these samples were especially prepared using a naphtha which had been distilled to ensure that the FBP was no higher than 190°C. The oil sands was a low grade sample containing about 7 w/w% bitumen and 35 w/w% fines (<44 μm).

In order to determine the drying curve in the region of most interest it is necessary to analyse samples for solvent and moisture content close to the 'dry' point. While the determination of water represents no significant problems the measurement of naphtha necessarily requires a certain amount of qualitative judgement. The reason for this is that any residual bitumen present in the sample contains components which have similar characteristics to naphtha. Consequently as the dry point is approached the uncertainty of the naphtha determination increases. A number of different analytical approaches have been used in an attempt to overcome the problems associated with naphtha analysis.

Experimental

Sample preparation

On the recommendation of the project consultants agglomerates were prepared from a low grade oil sand (from the Suncor overburden bench) and a naphtha sample distilled to remove any material boiling over 190°C. The composition of the oil sands used is listed below:

	(w/w %)
Solids	84.3
Water	8.2
Bitumen	7.1
Unaccounted	0.4
Fines (<44 μm)	34.5

As a result of the limited availability of the distilled naphtha fraction it was necessary to prepare the samples in three batches rather than using the larger scale continuous agglomerator. Each batch size was 0.8 kg and water was added to give a water to solid ratio of about 0.110. Extraction was carried out with a 20 w/w% solution of bitumen in the distilled naphtha. Pulp consistency was 50 w/w% (solids plus water as a percentage of the total charge).

Material was charged into a drum 18 cm diameter by 21 cm long in the order: oil sands, water and finally extractant solution. A number of mixing rods were added and the drum rotated at about 30 percent of the critical speed for 10 minutes. After solids agglomeration the bulk of the liquid was decanted through a 28 mesh screen in a Buchner funnel before transferring the solids to the filter. The solids were then drained under vacuum for 1 minute. The drained solids were then washed under vacuum with dilute bitumen solution (1 x 500 mls) and fresh solvent (1 x 500 mls) with a 1 minute drain between each wash.

The washed and drained agglomerates were transferred to a 1 gal. can and homogenised as well as possible. Three samples were taken for analysis and stored in a freezer until needed.

Analytical Techniques

1. Solids, Water, Bitumen and Naphtha by the Classical Technique

This technique requires 50-100 g. of sample, thus it could only be used to analyse the original, undried agglomerates (only 10-15 g of dried sample were available for test purposes). The method comprises extraction of the sample with hot toluene in a solids extraction apparatus. Water is separated from the reflux stream in a side arm trap while bitumen and naphtha are dissolved and collected in the distillation flask. This solution was analysed for bitumen by a colorimetric technique using bitumen solutions of known concentration as standards. The extracted solids are dried and determined gravimetrically. Naphtha can then be estimated by difference.

The colorimetric technique is very sensitive to the asphaltene content of bitumen and assumes that this component has the same concentration in the residual bitumen as in the standard bitumen. However, there is evidence that a poor bitumen solvent, like naphtha, selectively extracts non-asphaltene components which would make the residual bitumen richer in asphaltene. Consequently the colorimetric method tends to overestimate the residual bitumen content.

Two of the original samples of wet agglomerates were analysed by this method:

Sample #	1	2	Average
Solids (w/w %) -	72.59	72.37	72.48 ± 0.16
Water (") -	7.65	7.52	7.59 ± 0.09
Bitumen (") -	1.06	1.00	1.03 ± 0.04
Naphtha (") -	18.70	19.10	18.90 ± 0.28

2. Moisture Determination

Moisture content was determined by amperometric titration using a Fisher model 392 Karl-Fischer accessory with an automatic titrator and methanol as the solvent. Karl-Fischer reagent was standardised using weighed amounts of water injected directly into the cell from a syringe. After loading fresh, dried

methanol into the cell it was necessary to neutralise any residual water with Karl-Fisher reagent. Weighed samples of agglomerate were introduced directly into the cell and mixed to extract the moisture into the methanol. The extracted water was then titrated directly against standardised reagent. Water concentration was then calculated as follows:

$$C = \frac{V \times T}{W}$$

where C = concentration of water in sample (w/w %), V = volume of reagent (mls), T = reagent titre (mg H_2O/ml reagent) and W = weight of sample (mg).

All samples were measured in duplicate and the reagent was standardised weekly. For result summary see Table I.

3. Naphtha Content from Carbon Analysis

Total carbon contents of samples can be readily and precisely determined using a carbon analyser, such as the LECO CR12. In this equipment samples are burnt at high temperature in an oxygen atmosphere; the combustion gases are dried and then passed through an infra-red analyser which determines the carbon dioxide content at any instant. Integration of this data allows the total carbon content of the sample to be determined.

The problem with this technique is that it cannot distinguish between carbon derived from different sources i.e. naphtha and bitumen. However, this drawback can be overcome by determining the carbon content of a 'dry' sample. The difference between the measured carbon contents of 'wet' and 'dry' samples (all values recalculated on a dry basis) gives the carbon content due to naphtha. Knowledge of the carbon content of naphtha then allows the actual naphtha concentration in a 'wet' sample to be calculated.

In order to determine the 'dry' point a series of samples, dried for different times, were examined by head space GC. Each solid sample was sealed in a vial and equilibrated at an elevated temperature, up to 190°C. A sample of the vapours in the headspace of the vials were then injected into a GC and the resulting chromatograms examined. Samples showing no peaks on the chromatogram were considered to be completely devolatilised. Two samples were selected, one of which showed traces of the heavy components of naphtha while the other had a chromatogram typical of certain volatile bitumen components. These two samples therefore appeared to bracket the true 'dry' point. Carbon contents were determined for both samples and the average value was used for estimation of naphtha carbon in 'wet' samples.

The chromatograms indicated that for nearly 'dry' samples the residual naphtha comprised only the highest boiling naphtha components. A sample of the heavy naphtha components was

therefore analysed for carbon content to allow naphtha carbon to be converted to naphtha.

Dried samples were often found to have carbon contents less than the value determined at the 'dry' point. This was taken to mean that some bitumen had been volatilised during drying. The amount of bitumen recovered in this way was again determined by difference and the carbon content of bitumen. Also, the bitumen content of the original sample could be determined from the difference between the carbon content at the 'dry' point and the carbon content of a sample from which all the bitumen had been extracted with toluene.

4. Naphtha Content by Difference

The availability of a technique for determining the 'dry' point allows the total volatiles to be measured gravimetrically. Drying conditions were determined which allowed removal of the naphtha and water without materially affecting the bitumen content. A period of 16 hours at 100°C was found to be suitable. Thus knowing the moisture content and total volatiles (naphtha plus water) the naphtha content can be estimated by difference. This method is most applicable for higher moisture and naphtha contents (>1 w/w% of each component).

5. Naphtha Content by Multiple Extraction Head Space GC

This is a method of quantifying data obtained by head space GC. The technique is particularly suitable for determining the amount of a volatile component associated with a solid matrix

without having to extract that component. A sample is sealed in a vial and equilibrated at an elevated temperature. A portion of the headspace vapours are then injected and the total area counts determined. The vial is depressurised, resealed and then reequilibrated at the same temperature and an area count corresponding to the new vapour equilibrium determined. This procedure is repeated several times. It is not necessary to carry out an exhaustive extraction (i.e. until all volatiles are eliminated) because the decrease in volatile concentration follows the mathematical relationship of a first order reaction. The sum of peak areas, corresponding to the total amount present, can therefore be calculated from several successive determinations.

For a first order reaction the decrease in concentration of a component with time is proportional to the prevailing concentration:

$$\frac{-dC}{dt} = kC \qquad (1)$$

where C is the concentration, t is time and k is a constant. The concentration at any time (C_i) depends on the initial concentration (C_o):

$$C_i = C_o e^{-kt} \qquad (2)$$

If the gas extraction is performed stepwise at equal time intervals, the time t may be replaced by n-1, where n is the number of extraction steps. Also, as peak area is proportional to concentration, C_o can be replaced by A_1, the peak area from the first extraction step, thus:

$$A_i = A_1 \, e^{-k^*(n-1)} \qquad (3)$$

where k* is a constant including some instrumental parameters. Rewriting equation (3):

$$\ln Ai = k^* \, (n-1) + \ln Ai \qquad (5)$$

which is a linear equation of slope -k*. The value of k* can therefore be determined by linear regression from a few (3-5) points.

The total amount of volatile component is determined by the sum of all peak areas to exhaustion of the component. This sum can be represented by the following geometric progression:

$$\Sigma A_i = A_1[1+e^{-k^*} + e^{-2k^*} + \ldots + e^{-(n-1)k^*}] \qquad (6)$$

which simplifies to

$$\Sigma A_i = \frac{A_1}{1-e^{k^*}} \qquad (7)$$

Thus knowing A_1 and k^* the value of ΣA_i can be calculated.

In order to determine the actual concentration of a component it is necessary to carry out calibrations with known amounts of the component, preferably in the same kind of matrix as the actual sample. Concentration in the sample is then calculated based on simple proportionality.

The following instrumentation and analytical conditions were used for naphtha analysis of dried solids:

Instrumentation.

SIGMA 2000 GC with FID detector

Model HS-6 Manual Headspace Sampler

Model 3600 Data Station with Chrom-2 software.

Column.

Type: Chromosorb 101

Packing: 60 x 80 mesh

Dimensions: 6' x 1/8"

GC Conditions.

Column Temperature: 200°C, isothermal

Carrier gas:	helium
Flow rate:	25 ml/min at R.T.
FID Temperature:	250°C

Headspace Conditions.

Vial Temperature:	70°C.
Transfer Temperature:	200°C.
Thermostatting time:	60 min.
Pressurization time:	30 secs.

It is important to select the most appropriate naphtha cut for calibration purposes. This decision was made based on comparisons between the chromatograms obtained from the samples and from various naphtha fractions. Where the naphtha content was low (<1%) the high boiling naphtha standard was used, in all other cases the standard prepared from the whole naphtha seemed most appropriate.

Sample #	Naphtha (w/w %)				Bitumen (w/w %)		Water (w/w %)	
	Method				Method		Method	
	1	3	4	5	1	3	1	2
Orig. 1	18.7	-	-	-	1.06	0.7	7.65	-
2	19.1	16.3	19.5	-	1.00	0.7	7.52	7.27
3	-	12.8	15.8	-	-	-	-	7.84
3	IS*	ND**	NA‡	ND	IS	0.8	IS	0.46
4	"	"	"	"	"	0.8	"	0.43
5	"	"	"	"	"	0.9	"	0.44
6	"	"	"	"	"	0.9	"	0.44
7	"	"	-	"	"	1.0	"	0.33
8	"	0.6	0.9	?	"	1.0	"	0.84
9	"	ND	NA	ND	"	0.8	"	1.30
10	"	"	"	"	"	0.9	"	1.15
11	"	0.2	0.0	?	"	1.0	"	4.97
12	"	ND	NA	0→0.2	"	1.0	"	0.44
13	"	"	"	0→0.1	"	0.9	"	0.39
14	"	13.3	15.3	7.6	"	0.8	"	8.14
15	"	2.0	1.9	1.1	"	1.0	"	2.36
16	"	3.8	4.4	2.3	"	0.9	"	3.42
17	"	15.6	17.2	23.6	"	0.8	"	7.65

Table I: Summary of Analytical Data for Naphtha, Bitumen and Water (Solids to be determined by Difference.

* IS = Insufficient Sample

** ND = None Detected

‡ NA = Not Attempted, volatile content too low

? Chromatogram partially obscured by trace characteristic of waxes or resins. Naphtha could not be quantified.

Comments

Each of the analytical methods used has its limitations and as can be seen from the spread of the results there is some considerable uncertainty in the naphtha determinations, although the trends are quite clear in each series. Following are some comments which may be helpful.

Method 1: This method requires a relatively large sample and thus tends to give more representative results for the bulk material. Only the original, undried agglomerates were analysed by this technique.

Method 2: The K-F moisture determination is reliable and reproducible, results agreed well with those obtained in Method 1.

Method 3: This approach is most suitable for intermediate naphtha contents of about 1-5 w/w%. It is not precise enough to give good results where the naphtha is less than about 0.5%. At high naphtha levels problems with detector saturation, incomplete combustion and evaporation losses from very small samples make the method unreliable.

Method 4: Most reliable at high volatile content (>4 w/w%). Uses larger sample, therefore should give more representative results.

Method 5: Most sensitive technique but suffers from the fact that naphtha is not a pure compound and tends to fractionate

during drying. Consequently the accuracy of the method is very dependent on the selection of the most appropriate calibration standard. As an example there is a 100 fold difference between results calculated using the whole naphtha as the standard compared to those obtained using the highest boiling naphtha fraction. Also, at high naphtha contents there is a problem with detector saturation which requires that only very small (< 0.1 g) samples be used.

Recommendations

1) For undried samples use naphtha values obtained by methods 1 and 4. The differences observed between the results are likely due to sampling problems and solvent loss by evaporation over time.
2) In the case of samples 8, 15 and 16 there is not much to choose between any of the methods so that an average of all the available results is acceptable.
3) The chromatogram for sample 11 definitely indicates a small amount of naphtha, although it could not be quantified because of sample contamination. Thus the result obtained by method 3 should be used.
4) With samples 12 and 13 the general indications are that no significant naphtha is present.
5) All other samples not specifically identified above showed no trace of naphtha whatsoever.