IMPROVEMENTS IN MATERIALS HANDLING AND SAMPLING

The present invention concerns improvements in materials handling, more especially it concerns improvements in the sampling, and eventual analysis or assay, of variable feedstocks.

Many processes involve the sampling of bulk variable feedstocks, and this has especial importance where the feedstock contains one or more high value components. For example, in the recycle and refining of waste catalysts, or other wastes containing materials such as the platinum group metals, silver and gold, the refining organisation needs to determine levels of such metals in the bulk material to assess the value of metals to be credited to the owner of the bulk material. There is a need for improved sampling methods and, accordingly, for improved metal assays.

The bulk materials acting as feedstocks in the present invention may be in any non-gaseous form, for example liquid, such as waste homogeneous catalyst, solid or slurry. If the feedstock is a solid, such as a filter cake or other solid form, it is necessary to break up the solid, by for example crushing or milling so that the bulk is dispersible. Desirably, the particle size of solids is less than 500μm, preferably less than 100μm, bearing in mind the need to obtain suspension as a homogeneous slurry.

The present invention accordingly provides a method of refining comprising receiving a bulk sample of unknown composition, sampling the bulk sample to yield a reduced volume sample, assaying said reduced volume sample for one or more desired components, calculating the content of one or more desired components in the bulk sample, and passing the remaining bulk sample to a refining process; wherein sampling of the bulk sample comprises dispersing the bulk sample in a liquid, stirring the resulting dispersion in a mixing tank, continuously withdrawing from the bottom section of the tank a portion of the dispersion and recycling it via a recycle loop to the upper portion of the tank such that a substantially homogeneous dispersion is obtained in at least the recycle loop, and taking a representative sample of dispersion from the recycle loop. If necessary, the reduced volume

sample may be subsequently sub-divided and representative sub-division samples are assayed or analysed for key components in conventional manner.

Preferably, the refining process is a supercritical water oxidation process as described in WO 01/83834. For technical reasons, conventional refining techniques do not sample and assay the bulk sample, but only sample and assay after one or more preliminary concentration or refining steps. Accordingly, the present invention represents a significant departure from the state of the art, and is believed to offer advantages in speed of processing, and hence significantly reduce the cost of financing "work in progress".

The method of sampling according to the invention desirably uses a conical-ended stirred mixing tank, fitted with a pipe at the apex of the cone. Other tank shapes may, however, be used, for example a hemispherical, frusto -conical or similar section base. The recycle of dispersion is to the upper section of the tank, and may be made to any one or more points in said upper section. Conveniently, a single recycle point is approximately half-way along a radius of the tank.

Suitable mixing speeds, impeller shapes, recycle line diameters and recycle rates may vary according to the volume of the mixing tank and volume of the sample dispersion, and may be established by routine experiment. The aim is, of course, to ensure that the representative sample taken from the recycle loop is truly representative and this is essentially achieved by ensuring that the dispersion is homogenised.

Particularly preferred bulk sample feedstocks are spent catalysts, especially those comprising a platinum group metal carried on a carbon support. Such spent catalysts generally contain considerable quantities of organic solvent. However, since these are often regarded as wastes, they may be contaminated with a variety of organic (e.g. paper, cloth etc.) or inorganic (e.g. nuts and bolts etc.) matter. Such contaminating matter is desirably screened out.

Suitable liquid or slurry samplers are commercially available for use in the recycle loop. The volume taken is not especially important.

The methods used for assay or further analysis are conventional and form no part of this invention. Similarly, refining methods may be conventional or the supercritical water method of WO 01/83834.

Depending upon the nature of the bulk sample and especially the nature of solvents or residues associated with the values in the bulk sample, an additive to improve dispersion in the liquid may be required. The liquid is advantageously water, and conventional and commercially available surfactants may be used if the bulk sample is essentially non-polar. Initial tests on bulk samples which have a polar character indicate that certain surfactants, e.g. "Quadralene"™ (used for glassware washing machines) may be advantageously used.

Suitable concentrations of bulk sample in the liquid are from 10-15 wt%. Conveniently, the bulk sample, crushed or milled if necessary, is added, together with an appropriate surfactant, to the tank already charged with water, mixing is begun and the recycle initiated.

The present invention will now be described by way of example only and with reference to the accompanying drawings in which;

Figure 1 shows a schematic representation of apparatus for carrying out sampling according to the invention; and,

Figure 2 is a graph comparing metal values for a range of samples evaluated using the method of the present invention with those obtained using conventional pyrolysis.

With reference to Fig. 1, apparatus for carrying out the invention includes a mixing tank, 1. In proving trials, a steel tank of 600 litre capacity, with a conical bottom, has been

used. A conventional axial impeller, 2, is fitted in tank 1, to mix the contents. A recycle line, 3, of 19mm internal diameter is attached to the conical base of tank 1.

The recycle line is connected to a pump, 4, before being returned to the upper section of tank 1. The pump has been operated at 4400 l/hr. Fitted downstream of the pump is a commercial liquid/slurry sampler "Isolock"™ 5, which collects a sample volume of 500ml.

The recycle line may include a line, 6, to allow the contents of the tank to be emptied or further processed.

The charge of bulk sample is conveniently received in a bulk container, 7, fitted with a pump, 8, for water, wash water and/or surfactant. The bulk sample is fed to a screen, 9, to remove gross contaminants; a screen size of 3-10mm size is generally appropriate for spent carbon-based catalyst.

The sample is suitably passed to an assay laboratory, where it is resuspended and kept agitated. Sub-samples may be taken by using tube sampling. It is generally good practice to take a number of samples, some of which may be retained as a reference sample, to minimise the opportunity for process variability.

For example, where the bulk sample consists essentially of spent carbon-supported catalyst with organic solvent, it is preferred to oxidise all organic/carbonaceous material to CO_2, using a mixture of sulphuric and nitric acids. The residual precious metal can then be dissolved in a pre-set volume of aqua regia and analysed, for example using Inductively Coupled Plasma Emission Spectroscopy against standard solutions of known platinum group metal content.

EXAMPLE

Fifty-one catalyst samples were evaluated using the method of the invention. The samples were sourced from a wide range of used and unused materials with a range of physical properties and impurities. Results are shown in Table 1. Recovery is measured as the ratio (expressed as a percentage) between the amount of metal evaluated in each sample using the method of the invention and that evaluated by conventional pyrolysis. Excellent agreement was found between the two methods indicating that method of the invention provides an accurate and reliable measure of total metal content. The results of Table 1 are illustrated graphically in Fig. 2, with a line of unit gradient for reference.

It will be appreciated by the skilled person, that the method and apparatus as described may be varied in many ways. The invention includes all novel items and novel combinations and equivalents thereof. The skilled person may readily adapt the description herein in order to optimise the invention for particular circumstances.

Table 1.

Sample No.	Recovery/%	Sample No.	Recovery/%	Sample No.	Recovery/%
1	100.6	18	102.0	35	92.3
2	100.7	19	96.6	36	100.7
3	96.3	20	103.6	37	96.2
4	98.5	21	94.0	38	95.6
5	103.5	22	100.0	39	104.7
6	180.4	23	94.9	40	105.7
7	128.6	24	92.4	41	106.7
8	99.5	25	191.1	42	96.7
9	94.2	26	98.6	43	104.9
10	106.7	27	95.0	44	101.8
11	101.0	28	103.2	45	94.3
12	96.7	29	92.6	46	109.1
13	94.5	30	67.6	47	103.3
14	94.7	31	99.0	48	105.3
15	99.8	32	105.2	49	118.4
16	96.3	33	104.5	50	92.1
17	101.4	34	39.9	51	97.0

CLAIMS

1. A method of refining, the method comprising receiving a bulk sample of unknown composition, sampling the bulk sample to yield a reduced volume sample, assaying said reduced volume sample for one or more desired components, calculating the content of one or more desired components in the bulk sample, and passing the remaining bulk sample to a refining process; wherein sampling of the bulk sample comprises dispersing the bulk sample in a liquid, stirring the resulting dispersion in a mixing tank (1), continuously withdrawing from the bottom section of the tank a portion of the dispersion and recycling it via a recycle loop (3) to the upper portion of the tank such that a substantially homogeneous dispersion is obtained in at least the recycle loop, and taking a representative sample of dispersion from the recycle loop.

2. A method according to claim 1, wherein the bulk sample is a spent catalyst.

3. A method according to claim 2, wherein the spent catalyst is a platinum group metal on carbon catalyst.

4. A method according to any one of the preceding claims, wherein the liquid is water.

5. A method according to any one of the preceding claims, where a surfactant is added to the liquid or the sample to facilitate dispersion.

6. A method according to any one of the preceding claims, wherein the sample is a solid having particle size of less than 500μm, preferably less than 100μm.

7. A method according to any one of the preceding claims, wherein the refining process is a supercritical water oxidation process.