

Method of estimating crude tall oil (CTO) in black liquor

Scope

This is an analytical method for the estimation of tall oil in Kraft black liquor. This method involves the extraction of the oil from an aqueous-alcohol-acetone solution in which the acidified liquor residues are soluble.

Apparatus

1. Buret, 50-mL capacity with 0.1 mL divisions.
2. Pipets, 10-mL and 100-mL.
3. Graduated cylinders, 10-mL, 100-mL and 250-mL.
4. Beakers, 400-mL and 100-mL capacity.
5. Separatory funnels, two 500-mL.
6. Sample container, 1 pint or larger, glass or polypropylene.

Reagents

1. H₂O₂ Solution - Mix 3 volumes of commercial 30% H₂O₂ with 2 volumes of water.
2. Na₂SO₃ - Dissolve 20 g of anhydrous Na₂SO₃ in 100 mL of water.
3. HCl (1:1) - Dilute conc. HO with an equal volume of water.

NOTE 1: For safety, add the acid to the water, not water to the acid.

4. Acetone - methanol - Add 1 volume methanol to 4 volumes acetone. Mix well.
5. Water-acetone-methanol - Mix 2 volumes of acetone, 1 volume of water and 1 volume of methanol.
6. Petroleum ether, boiling range 40-60°C.
7. Isopropanol, neutralized to a phenolphthalein end point.
8. Standardized alcoholic KOH solution, 0.05N - maybe prepared by 1:10 dilution of standardized 0.5 N alcoholic KOH.

9. Phenolphthalein indicator solution in ethanol (1%).

Procedure

Note 2: The sample must be representative of the process for this test to be of any value. Sampling lines (particularly those near skimmers) must be cleared of my accumulations of soap or other debris by opening the s^omilling line for several seconds before collection. The sample should be collected directly into water to give an approximate solids concentration of 5%.

1. Estimate the solids concentration of the liquor stream to be sampled. Calculate the volume of black liquor required to give an approximate 5% solids concentration in a measured and marked container.
2. Calculate the amount of distilled water required for the 5% solids concentration and fill the container with that amount of distilled water. Mark the container where the total volume will be after the calculated volume of black liquor has been added.
3. Sample the black liquor directly into the water filling it to the mark made in step 2.
4. Determine the total solids content by drying 10 mL of the dilute sample prepared in step #1 in a tared crucible at 105° t 5°C for 24 hours. Alternatively, determine the solids with a moisture balance.

NOTE 3: If the soap content of the liquor is low, the sample volume may be increased. The volumes of the reagents used in steps 5- 7 and the value of D in the calculation should be similarly increased.

5. Pipet 100 mL of the dilute sample into a 500-mL separatory funnel. Add 5 mL of H₂O₂ solution and shake vigorously for 45 seconds, venting the funnel intermittently.

6. Within 1 minute after adding HO, add 5 mL Na₂SO₃ solution. Shake and vent for 1 minute.
7. Acidify by adding 10 mL of the 1:1 HCl. Shake and vent intermittently for 1 minute.
8. Add 250 mL of the acetone-methanol, and mix thoroughly for 30 seconds (to dissolve the lignin). Occasionally a precipitate is found that does not redissolve. Note this, but proceed with the test.
9. Add 150 mL of petroleum ether, then shake and vent for about 2 minutes.
10. After shaking, allow about 5 minutes for the phases to separate. Transfer the lower phase to a second 500-ml, separatory funnel.
11. Wash the petroleum ether phase in the first separatory funnel twice with 25 mL portions of the water-acetone-methanol mixture and add the washings to the aqueous phase in the second separatory funnel.
12. Pour the washed petroleum ether extract into a 400 mL beaker. Start evaporating the petroleum ether by placing the beaker on a steam bath at 80°C.

NOTE 4: Do not use a hot plate for this evaporation. Petroleum ether vapors could result in a fire.

13. Extract the phase in the second separatory funnel with 100 ml, of petroleum ether. Draw off the lower phase, leaving the petroleum ether in the separatory funnel.
14. Wash the ether twice with 25 mL portions of the water-acetone-methanol. Allow the phases to separate after each wash and discard the water-acetone-methanol phase after each wash. Combine the washed petroleum ether phase with the original petroleum ether extract in the 400 ml, beaker on the steam bath.
15. Evaporate the petroleum ether extract over a waterbath at 80°C until just the oil appears on the bottom portions of isopropyl alcohol and pour them over the filter of the beaker. Add 25 mL of neutral isopropyl alcohol to redissolve the oil.
16. Filter the dissolved oil through coarse filter paper or coarse glass frit into a 100 mL beaker. Wash the 400 mL beaker thoroughly with additional paper or frit.

Then wash the filter paper with isopropyl alcohol until the final filtrate volume is approximately 50 mL.

17. Add 1 mL of 1% phenolphthalein indicator solution and titrate with 0.05 N alcoholic KOH solution. The endpoint is taken at the point where the first pink color persists for 30 seconds.

Calculations

1. Assuming an acid number of 160, calculate the weight of tall oil present.

$$\text{Weight Tall Oil, g} = \frac{A \times N \times 56.1}{160}$$

where:

- A = mL KOH used
- N = normality KOH solution
- 56.1 = equivalent weight of potassium hydroxide

NOTE 5: When the actual acid number for the CFO being produced is known, the actual acid number should be used in place of the assumed acid number.

2. Calculate percent tall oil on liquor solids basis using weight of tall oil calculated above.

$$\text{Percent Tall Oil on Liquor Solids Basis} = \frac{C \times 10}{D}$$

Where:

- C = weight of tall oil, grams
- D = solids in 10 L dilute black liquor, grams.