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Solvent Refining of Low Temperature Tar
With Paraffinic Solvents

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Commercial refining of coal tar is based on a primary separation involving either atmospheric or vacuum distillation. The tar is separated into a distillate fraction and a non-volatile pitch fraction. The high molecular weight character and thermal instability of most tars limits the amount of distillate from 50 to 60% of the raw tar. These factors have influenced the utilization of tar to a considerable extent.

Solvent refining of tar is of interest as an alternate primary fractionation method since it might overcome the major limitations of the distillation process. The temperatures required for solvent refining are usually considerably lower than the maximum temperatures reached in distillation and consequently less destructive to the thermally sensitive tar components. In addition, separations based on chemical structure can be effected depending on the choice of solvent.

Low temperature coal tar is composed of an extremely broad and complex mixture of tar acids, nitrogen bases, sulfur compounds, neutral hydrocarbons in various degrees of unsaturation or cyclization and heterocyclic structures. It was therefore of interest to determine what separations were possible by solvent refining.

The results of earlier investigators on solvent refining of coal tars can be divided into two categories depending on the class of solvent used. Extractions carried out by Sinnatt^(1,2) with polar solvents including methanol, ethanol, pyridine, etc., resulted in essentially complete solubility of the tar. Extraction of tar with paraffinic hydrocarbons, pentane to decane, carried out by Jacobsen⁽³⁾ and Weindel⁽⁴⁾ resulted in the solution of 40 to 60% of the tar. There have been no studies reported on the refining of raw low temperature coal tar with low boiling paraffinic hydrocarbons under pressure which would permit an evaluation of the important extraction variables.

Kuhn⁽⁵⁾ examined the propane refining of a pentane extract from high temperature tar. This extract represented 38% of the raw tar. At extraction temperatures of from 30 to 90°C yields of propane extract varied from 5 to 72% of the pentane soluble tar. The yield of extract was essentially independent of temperature varying directly with the solvent ratio. The separation effected by propane appeared to be principally on the basis of molecular weight. In addition, oxygen, nitrogen and sulfur containing compounds concentrated in the propane reject.

In our investigation, a study was made of single-stage batch extraction of low temperature coal tar with paraffinic solvents from propane through hexane. An apparatus was designed in which extraction of tar or tar fractions could be made over a wide range of temperatures and which permitted precise material balances. The effect of solvent molecular weight, solvent structure, solvent ratio and extraction temperature has been correlated with the yield and composition of extract and raffinate tars.

EXPERIMENTAL

The extraction apparatus consisted of a 2-liter capacity Parr stirred autoclave modified as shown in Figure 1. The bottom of the bomb was equipped with a 1/4-inch stainless steel valve and drain tube to provide bottom withdrawal of the liquid contents. This permitted the reactor to be used as a pressure separatory funnel. An autoclave skin thermocouple was employed in addition to the inner thermocouple to prevent excessive bomb surface temperature which might polymerize the thermally sensitive tar components. To keep the viscous pitch fluid and mobile, the drain tube was provided with a nichrome heating element. This tube extended into a round bottom flask which served as the product receiver and flash still. A water-cooled condensing system followed by a dry ice trap condensed the flash distilled solvents. Propane, butane and pentane were charged to the reactor from the transfer bomb by nitrogen pressure. Recovery of the more volatile solvents was measured by the wet test gas meter.

The autoclave was charged with 250 to 600 gms of filtered Disco tar which contained 2.0% moisture. The tar volume was calculated as moisture-free with a specific gravity at 25/25°C of 1.100. The amount of solvent to be added was computed, the required amount volumetrically measured, weighed and chilled to -20°C to minimize solvent loss in transfer to the opened autoclave. However, the more volatile solvents, propane, butane and pentane, were charged to the assembled reactor quantitatively by weight difference from the nitrogen pressurized transfer bomb. After the reactor was sealed, the inner bomb temperature was brought to the desired level in approximately one hour and the temperature held constant during agitation for 15 minutes. Separation of the phases by gravity settling was allowed for 1/2 hour. The lower phase (pitch or raffinate phase) was drawn off through the heated drain tube and appeared as a frothy gelatinous mass. The interface was recognized when a sudden burst of gas was emitted from the drain tube due to the flash vaporization of the volatile solvent-rich extract phase. At this time the gelatinous frothy nature of the draining liquid disappeared. For collection of the extract phase, the receiver was replaced by a clean one and the extract tar and flashed solvent collected separately. Further separation of solvent from the product was done by fractional distillation. Propane and butane recovery was measured by a wet test gas meter. Overall material balances ranged from 98 to 100%. All solvents used were 95% or higher in purity except pentane which was a commercial grade of 90% purity.

DISCUSSION OF RESULTS

The yield of extract tar is dependent upon three factors, that is, the intrinsic solvent properties, solvent ratio and temperature. If the temperature is maintained constant at 100°C and extract yield is plotted against solvent ratio, extract yield increases with increased solvent boiling point or carbon chain length as shown in Figure 2. Thus at a solvent ratio of 2.5 n-butane yields 42% extract, n-pentane 57% and hexane 70%.

The branched chain solvents behave more like a lower molecular weight straight chain analogue, for example, the yield of extract using isopentane, falls between the yields observed for n-butane and n-pentane. The branched paraffin, 2,3-dimethyl butane, in a similar comparison yields 62% extract, a value between the yields for n-hexane and n-pentane. Thus, if the boiling points of the solvents are plotted against extract yield at a solvent ratio or 2.5, the relationship is very nearly defined by a straight line function.

At a constant temperature of 100°C a solvent ratio greater than 2.5 has very little effect upon yield. This is particularly true of the solvents boiling above n-butane. When the hexane ratio is decreased below 2.5 the yield of extract increases to 78% at 0.75 solvent volumes. Decreasing the solvent ratio further results in slow and uncertain phase separations. It is estimated that complete solubility of the tar, that is, the plait point is attained at a solvent ratio of 0.6. Pentane behaves in a similar manner, however, the plait point is somewhat lower and is estimated at a solvent ratio of 0.5. Lowering the butane or propane solvent ratio below 2.5 results in a reverse effect on yield in contrast to that obtained with pentane and hexane. The yield of extract using butane drops to 37% at a solvent ratio of 1.

The effect of temperature upon the yield of extract tar obtained with hexane and butane is summarized in Figure 3. The higher temperature produces a considerable increase in yield. Thus at a solvent ratio of 2.5 the yield at 100°C of 71% is increased to 78% at 150°C. Butane in comparison exhibits the reverse effect with temperature and gives lower yields at the higher temperature. By raising the temperature from 100°C to 150°C the yield at a solvent ratio of 2.5 decreases from 44 to 43%. At a solvent ratio of 4.5 this decrease in yield with increased temperature is even more pronounced and drops from 51 to 44%. This decrease in yield with butane at the higher temperature may be attributed to the low critical temperature of butane (153°C) for at 150°C butane approaches the completely gaseous state. Hexane exhibits the more normal liquid solvent behavior because at 150°C it is below its critical temperature of 235°C. Pentane shows the same effect of temperature as hexane. Similar results were obtained by Kuhn⁽⁵⁾ on propane extraction of pentane extract from high temperature tar. Kuhn showed that the yield of extract was directly proportional to the solvent ratio and essentially independent of the temperature.

The efficiency and selectivity of fractionation of the tar by the solvents was measured by the ability of the solvent to produce an extract of low asphaltene content. Asphaltenes were measured as that fraction of the extract tar sample which was insoluble at 25°C in 120 volumes of petroleum ether, which had a boiling range of 30-65°C. The feed tar contained 24.8% asphaltenes. The asphaltene contamination of the tar extract fractions with temperature, solvent, and solvent ratio as parameters was determined and is shown in Figure 4. Increase in extraction temperature shows that a particular solvent became less selective as indicated by the increased asphaltene contamination of the extract. For example, hexane at 150°C shows an extract tar asphaltene contamination of about 23% and only 18% at 100°C. A similar broad change is noticed with pentane and butane. The lower the boiling point of the solvent, the greater selectivity it exhibits at a given temperature and solvent ratio. Thus, at 100°C, hexane is the least selective and butane the most.

Increasing the solvent ratio from 1 to 2.5 produces the largest increase in selectivity. Increasing the hexane ratio from 1 to 2.5 at 100°C results in a reduction in asphaltenes from 18 to 12%. Pentane and butane show similar changes. Increasing the solvent ratio above 2.5 produces little change in the solvent selectivity as indicated by the relatively constant asphaltene values. However, at 150°C hexane selectivity appears to increase as the solvent ratio is increased above 2.5.

Because of the economic value of low boiling tar acids in tar processing, it was important to compare the solvents with respect to their ability to recover the tar acids boiling to 230°C. A comparison of the recovery of tar acids boiling to 230°C and the asphaltene carryover in the extract was made for propane, butane, pentane and hexane with the extraction temperature held constant at 100°C and the solvent ratio of 2.5, Figure 5. Recovery of tar acids boiling to 230°C increases with increased carbon chain length of the solvent. Thus, propane gives the lowest recovery, 23%, and hexane the highest, 69%. However, the higher boiling solvent shows a poorer selectivity by higher asphaltene carryover.

To determine if multi-stage extraction would increase the low boiling tar acid recovery, reject pitch from the one-stage extraction was contacted a second time with fresh solvent. The extraction was carried out at 100°C with pentane at a solvent ratio of 2.5. By this second extraction the total recovery of tar acids boiling to 230°C is increased to 78.5%. It is estimated that 5 stages are sufficient to give recoveries better than 95%.

Comparison of the ultimate analyses of extracts and pitches obtained at 100°C at a solvent ratio of 2.5 in Table I indicates that the more polar and hetero-atom compounds are preferentially rejected and concentrated in the pitch phase. The concentration of nitrogen, oxygen and sulfur is much lower in the extract. Compounds rich in hydrogen and the lower molecular weight compounds are concentrated in the extract. As the molecular weight of the solvent decreases, the selectivity for hydrogen rich components increases as evidenced by the increase in hydrogen content of the extracts. The selectivity for rejecting sulfur compounds is independent of solvent molecular weight.

Comparison of some of the properties of the extracts and rejects in Table II further shows the type of tar fractionation effected by the solvents. The extracts consist of the lower gravity, the higher hydrogen carbon ratio and lower viscosity tar components, that is, the lower molecular weight compounds. In passing from propane to hexane, each successively higher boiling solvent is fractionating the tar at some higher molecular weight cut point. This is borne out by the progressively increasing extract viscosity and increased softening point of the reject fraction.

A comparison of the fractional distillation analyses of the extracts shown in Figure 6 indicates that the solvents are fractionating the tar not only with respect to functional group components but also with respect to molecular weight or distillation cut point. As the carbon chain length of the solvent is increased, the distillation (analysis) of the extract approaches that of the feed tar. Thus, propane extract contains the least pitch (>350°C) and hexane extract the most. Since the amount of each distillate fraction boiling below the pitch fraction is greater than the corresponding feed tar fraction, it is indicative that solvent fractionation resembles fractional

distillation; however, the cut point corresponds to a higher temperature than obtainable by conventional fractional distillation. This cut point varies with the intrinsic solvent nature and increases with the increased boiling point of the paraffinic solvent employed. Thus, butane exhibits a higher cut point with respect to distillation than propane. Pentane is higher than butane, and the branched chain solvents behave more like the lower molecular weight straight chain analogues.

SUMMARY

1. An apparatus was designed which permitted extraction of a viscous tar with paraffinic hydrocarbon solvents over a range of temperatures with accurate phase separations and material balances.
2. Solvent ratios higher than 2.5 did not appreciably increase the yield of extract or extraction selectivity with solvents boiling above n-butane. Propane and n-butane differed from the higher boiling solvents in that yield of extract was proportional to the solvent and these solvents exhibited the highest selectivity.
3. Solvents boiling above n-butane showed higher yields but lower selectivity upon increasing the temperature. Normal butane extractions showed very little effect of temperature.
4. Extraction of low temperature tar was comparable to distillation in that, the higher molecular weight, higher boiling compounds were preferentially separated as a reject phase.
5. The depth of extraction, comparable to distillation cut point, was dependent upon the boiling point of the solvent employed. The higher the boiling point of the solvent the deeper was the cut point. The depth of extraction obtainable by solvents was at a higher molecular weight level than possible by conventional distillation.
6. High recovery of low boiling tar acids should be possible in a multi-stage extractor.

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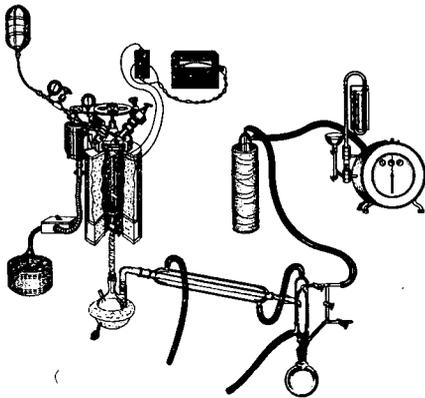


Figure 1

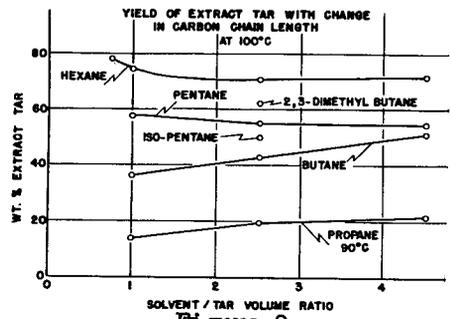


Figure 2

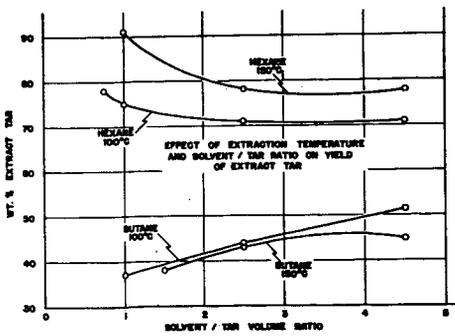


Figure 3

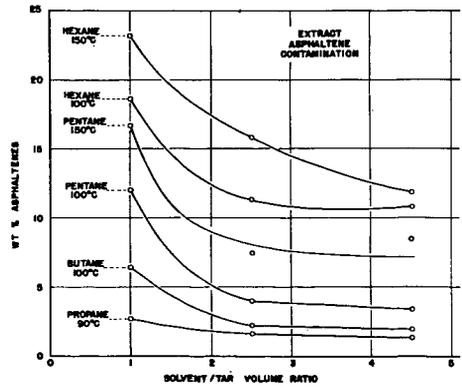


Figure 4

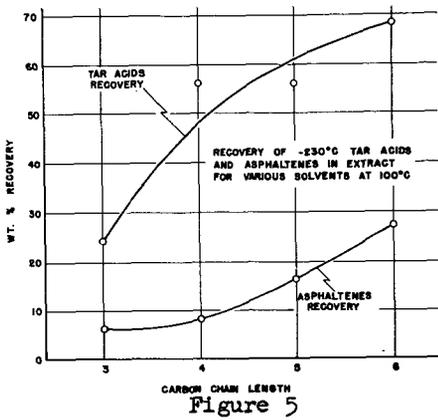


Figure 5

TABLE I

ULTIMATE ANALYSES

| SOLVENT | EXTRACTS | | | |
|-------------------------|----------|----------|-----------|----------|
| | PROPANE | n-BUTANE | n-PENTANE | n-HEXANE |
| SOLUBLE FRACTION | | | | |
| H | 7.09 | 9.77 | 6.40 | 8.29 |
| C | 82.89 | 84.92 | 84.86 | 85.51 |
| N | 0.97 | 0.20 | 0.39 | 0.49 |
| O | 6.76 | 4.96 | 5.49 | 4.85 |
| S | 1.8 | 0.75 | 0.74 | 0.86 |
| REJECT FRACTION | | | | |
| H | 6.96 | 6.60 | 6.51 | 6.68 |
| C | 83.28 | 81.14 | 80.81 | 80.68 |
| N | 0.98 | 1.05 | 1.26 | 1.34 |
| O | 7.84 | 6.54 | 10.8 | 9.92 |
| S | 1.04 | 1.19 | 1.38 | 1.27 |

TABLE II

COMPARISON OF PROPERTIES

| SOLVENT | EXTRACTS | | | |
|--------------------------|----------|----------|-----------|----------|
| | PROPANE | n-BUTANE | n-PENTANE | n-HEXANE |
| SOLUBLE FRACTION | | | | |
| SPEC. GRAY. 25/25°C | 1.10 | 0.974 | 1.084 | 1.043 |
| n/0 | 1.02 | 1.29 | 1.18 | 1.18 |
| VISCOSITY S.U. SEC. 100% | 84.5 | 83.6 | 100.8 | 124.7 |
| REJECT FRACTION | | | | |
| FIXED CARBON | 7.84 | 7.94 | 8.24 | 8.24 |
| n/S | 1.02 | 0.98 | 0.97 | 0.98 |
| RED. V. ORSA. ° | 30.0 | 31.0 | 31.5 | 32.0 |

DISTILLATION OF EXTRACT TAR

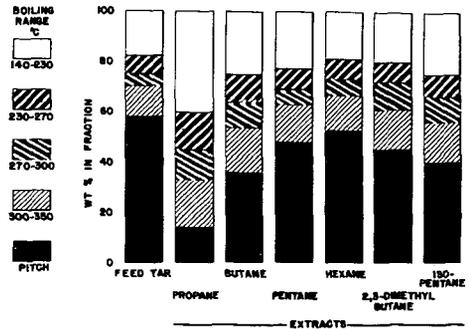


Figure 6