Manufacture and Use of Solid Petroleum Pitch

Harold Beuther
Richard G. Goldthwait

Gulf Research & Development Company
Pittsburgh, Pennsylvania

INTRODUCTION

For many years there has been a continuing effort in the petroleum industry to increase the amount of distillate products obtained from crude oil. This effort has been motivated by the higher value of distillate oils and the poor economics of adding these higher value distillate oils to viscous residues to make them marketable as fuels. During the past decade some progress has been made on this problem. The residues from certain crudes can be processed effectively by thermal visbreaking to increase substantially the yields of distillate oils. The residues from any crude can be processed either by coking to make largely distillate oils and coke or by hydrodesulfurization to remove sulfur as well as to convert any required amount of the asphalt. In addition, many refiners today gain distillate yield by burning viscous residual oils as refinery fuel to avoid the blending-off of lighter oils required in the marketing of No. 6 Fuel Oil. The production and burning of solid petroleum pitch goes one step further than the use of a viscous residue. By concentrating further the heavy residual oils that the refiner now burns, additional distillate oil is removed and the asphaltic portion is converted to a hard, brittle solid which can be handled and burned as a solid fuel. There are several potential advantages in going to this added degree of reduction of petroleum residues. (1) A solid fuel can be stored and transported more easily than viscous fuel which requires heating to keep it pumpable when the fuel use is beyond the immediate refinery area. (2) The reduced yield of residual fuel when making a solid pitch results in a higher yield of more valuable distillate oil. While this distillate oil is "dirty" by normal standards for distillate stocks, improved refining techniques in modifications to catalytic cracking and in hydrocracking will now readily accept such oils as charge stocks. (3) The processing required to produce a solid petroleum pitch is more simple and less costly than is required for either coking or hydrodesulfurization.

DESCRIPTION OF SOLID PETROLEUM PITCH

Solid petroleum pitch is an asphalt concentrate from crude oil where enough oil has been removed from the asphalt to produce a high melting point, coal-like solid. This material is brittle and easily pulverized; it can be stored outside without fusing or agglomerating and makes an excellent solid fuel having considerable less ash and more BTU'S per pound than coal. Table I gives a brief summary of the physical properties of petroleum pitch compared to bituminous coal, a coal tar pitch and petroleum coke. Although not shown in this table, petroleum pitch is more similar to certain natural occuring bitumens, such as gilsonite than it is to coke, coal or coal tar pitch. Petroleum pitch differs from coal and petroleum coke in that it has a melting or softening point. This softening point is high enough, however, (about 350°F.) to allow pitch to be stored in 40-foot piles at 170°F. without the agglomerization of particles.

Needless to say, the advantage for producing a solid petroleum pitch from a crude oil will vary widely and will be most advantageous to those refiners having high asphalt-content crudes and in a depressed marketing area for residual fuel oils. In looking to the future, the need for such a process is expected to increase when our fuel economy must rely more heavily on low-gravity crudes, tar sands, and low grade hydrocarbon deposits.

Table I

PROPERTIES OF VARIOUS CARBONACEOUS SOLIDS

	Petroleum Pitch	Typical Bituminous Coal	Coal Tar Pitch	Petroleum Coke (Delayed)
Specific Gravity	1.05-1.15	-	1.20-1.30	1.28-1.42
Softening Point: °F.	300-400	-	110-320	none
Solubility in Benzene: %	75-99	-	45-75	-
Volatile Matter: %	50-70	34	40-50	8-17
Heating Matter: BTU/Lb.	16,500-17,600	14,400	-	14,600-16,000

MANUFACTURE OF SOLID PETROLEUM PITCH

It can been seen from the volatile content in Table I that petroleum pitch is a concentrate of the asphaltic material in crude. By removing or eliminating oil which is included with normal vacuum reduced crudes, a pitch can be produced whose asphaltene concentration is sufficiently high to impart hardness properties, which permit satisfactory handling, storing, grinding and burning as a solid fuel. For certain crudes which have very hard asphalts, it is possible to produce solid petroleum pitch by simply increasing the severity of normal refinery vacuum distillation[1] by 50° to 100°F. (corrected to 760 mm. Hg). Certain Mississippi and Venezuelan Crudes are of this type. Such crudes are generally low in API gravity and sufficiently high in viscosity to meet the No. 6 Fuel Oil specification upon removal of a few per cent of gasoline. Baxterville Crude, for instance, can be distilled to produce 5% gasoline with the remaining 95% being a heavy fuel oil. By a combination of atmospheric and vacuum distillations (the latter carried out at 1070°F. corrected to 760 mm. Hg), there is obtained from this crude 5% of gasoline, 24% of furnace oil, 46% of fair-quality catalytic cracking charge stock, and 26% of a 360°F. softening point pitch. A simplified flow diagram for one of several possible methods for carrying out this operation is given in Figure 1. By varying the severity of distillation, pitches of varying softening point can be obtained; however, higher softening point pitches are more difficult and costly to produce and the resulting gas oils are of higher carbon residues and metal contents. As will be discussed later, it is believed that pitches of 350°F. minimum softening point can be handled and burned in most burners designed for either coal or heavy fuel oil with but minor modifications, and it is entirely possible that lower softening point (275°-325°F.) pitches can be handled and burned in specially-designed equipment. Yields and inspection data for pitch and catalytic cracking charge stock produced at three severities of vacuum reduction from Baxterville Crude are given in Table II.

The use of vacuum distillation to produce pitch is limited to crudes containing asphalts of very low oil content (hard asphalts). For other crudes it is necessary to remove a portion of the oil from the asphalt by cracking. Thermal visbreaking of

Table II

YIELDS AND INSPECTIONS OF PITCHES AND CATALYTIC CRACKING STOCKS FROM SEVERAL SEVERITIES OF VACUUM REDUCING BAXTERVILLE CRUDE

	Mild Vacuum Reduction	Moderately Severe Vacuum Reduction[a]	Severe Vacuum Reduction
Pitch			
Yield: % by Vol. of Crude	33.5	25.7	17.9
Ring and Ball Softening Point: °F.	275	360	441
Catalytic Cracking Charge Stock			
Yield: % by Vol. of Crude	37.7	45.5	53.8
Carbon Residue, Conradson: %	0.64	1.58	3.32
Vanadium: PPM	0.13	0.70	3.40
Flash Temperature,[b] Corrected to 760 Mm. Hg: °F.	969	1068	1201

[a]Recommended reduction to produce a solid fuel.

[b]When charging a gasoline-free Baxterville Crude to vacuum tower.

the normal vaccum residue from many crudes concentrates the asphaltenes by "cracking out" the oil so it can readily by removed by atmospheric distillation.[2] Here again, when producing pitch by visbreaking, the asphalt charge to the visbreaker must be relatively hard, preferably above 160°F. softening point; otherwise a very severe visbreaking operation is necessary or the subsequent distillation must be carried out under vacuum. A typical operation to produce pitch from a 12.5% reduced Eastern Venezuela Crude (165°F. softening point) requires single-pass visbreaking at furnace conditions of 915°F. outlet temperature and 200 psig. pressure. Operating conditions in this range are practical for heavy vacuum reduced crudes[3] as evidenced by several visbreaking operations for conventional purposes now carried out in Gulf's refineries. By visbreaking a 5.2 °API vacuum reduced Eastern Venezuela Crude and distilling the visbreaker residue, the following yields of products are obtained: 13.3% gasoline and naphtha, 13.3% furnace oil, 15.6% catalytic cracking charge stock, 12.2% fuel oil, and 45.3% pitch. The inspections of the distillate products are similar to products obtained from delayed coking and are given in Table III. The process flow, which is shown diagrammatically in Figure 2, is typical of thermal visbreaking except for the handling of the visbreaking effluent. The visbreaker effluent is distilled at atmospheric pressure in the presence of 5 to 40 pounds of steam per barrel of charge to obtain an approximately 350°F. softening point pitch and a cracking stock, as well as lighter distillates. A more severe visbreaking operation would reduce the steam requirements.

Most Venezuelan Crudes and domestic crudes containing hard asphalts such as East Texas, California, etc., are very readily processed by visbreaking to produce solid pitch. Crudes with softer asphalts require more severe visbreaking and distillations conditions than those given above for the Eastern Venezuela residue, and high softening petroleum pitches have been prepared from Kuwait, West Texas, and Mid Continent Crudes.[4,5]

Table III

PRODUCTION OF PITCH BY THERMAL VISBREAKING
FOLLOWED BY ATMOSPHERIC REDUCTION
OF REDUCED EASTERN VENEZUELAN CRUDE

300°F. End Point Gasoline (10 RVP)	
Yields: % by Vol.	8.0
Sulfur: %	0.61
Research Octane No., +3 Cc. TEL	85.6
300°-400°F. Naphtha	
Yield: % by Vol.	5.3
Furnace Oil Fraction	
Yield: % by Vol.	13.3
Sulfur: %	1.83
Gravity: °API	31.2
Characterization Factor	11.34
Catalytic Charge Stock	
Yield: % by Vol.	15.6
Sulfur: %	2.02
Characterization Factor	11.62
Carbon Residue	0.8
Heavy Gas Oil	
Yield: % by Vol.	12.2
Carbon Residue, Conradson: %	13.9
Pitch	
Yield: % by Vol.	45.3
Softening Point: °F.	364

In the manufacture of pitch, it is necessary to provide a means of cooling and solidifying the pitch after removal from the atmospheric or vacuum distillation column. The most practical means for most locations is through the use of a continuous moving stainless steel belt. The hot pitch from the distillation column is poured continuously onto the belt, which is cooled from beneath by water and may be cooled with auxiliary water sprays on top. Pitch produced by this manner consists of flakes about one-quarter inch thick which break at random into pieces one to six inches across. The pitch readily separates from the stainless steel belt upon cooling because of its different coefficient of expansion. A photograph of pitch produced in this manner is shown in Figure 3. Such material is quite brittle and breaks readily upon handling. With handling there is produced only a very small amount of fines which are not troublesome. There are other methods which may be more desirable in certain locations for cooling and solidfying the hot liquid pitch. These include the use of large cooling pits into which the pitch is pumped as a hot liquid and allowed to cool slowly in the atmosphere in a large mass. When solid, the pitch is then broken up and moved with power shovels. Hot liquid pitch also may be solidified by spraying into water or steam, or it may be solidified on a water-cooled rotary drum. From our experience, however, the simplest and most convenient method is that of the continuous moving belt.

USES OF PETROLEUM PITCH

Because of the large quantities of crudes and residues processed in the petroleum industry, any scheme for producing solid petroleum pitch which would be effective in improving the ratio of distillate to residual oils would produce so much pitch that a fuel market must be considered as its primary use. Thus, it was on the basis of a fuel market that economics and process developments were carried out. Even a small unit charging 5000 barrels per day of Eastern Venezuela residue would produce 430 tons per day of pitch. In considering the use of petroleum pitch as a fuel it was necessary to determine the minimum softening point that would allow transportation, storage and grinding in hot weather without the pitch becoming tacky or plastic and possibly fusing. It was found that these properties of pitch depended on the crude source and method of production. For a typical pitch from Eastern Venezuela Crude, it was found that a 350°F. ring and ball softening point was sufficiently high to prevent fusion at temperatures and pressures which would be encountered under almost any circumstance. Figure 4 presents a plot of incipient fusion temperature of Eastern Venezuela pitch as a function of pitch softening point when under a pressure equivalent to 40 feet of pitch. This incipient fusion temperature is the temperature at which particles first adhere to one another but readily break apart with slight handling. From this plot it can be seen that a 350°F. softening point pitch only begins to fuse at 170°F. at these conditions. It is not until temperatures of about 15°F. higher that fusion becomes serious and permanent. Thus, an Eastern Venezuelan pitch of 350°F. softening point can be stored in piles 40 feet high at 170°F. before any evidence of particle adherence occurs. Obviously, lower softening point pitches would be satisfactory in locations with lower ambient temperatures. The burning characteristics of 350°F. softening point pitch have been evaluated in a two-foot diameter Babcock and Wilcox experimental cyclone furnace.[6]

Several modifications were made to the normal operation of the cyclone furnace.

1. Cold air was used in pulverizing and charging the pitch so it would not melt before entering the furnace.

2. An ash with a suitable fusion temperature was added to the pitch to form a fluid slag coating on the walls of the cyclone.

The ash which was added was from the burning of coal and the quantity, 5%, was chosen arbitrarily. This quantity could have undoubtedly been reduced or the slag could have been recycled if no such material were continuously available. The burning characteristics of the pitch were excellent in every respect. The flame was stable and clean, the appearance of the stack was excellent, and the oxygen content of the flue gas was 2% indicating about 10% excess air. There were no problems with ingition, dust carryover, or flame propagation. There was no build up of slag in the combustion chamber, and the burner itself was clean with no build up of pitch. The carbon loss to the stack was below that obtained with coal firing, which is in the range of one pound per 1000 pounds of flue gas. During the test, no particular effort was made to control the grinding of the pitch or the size of the slag particles. The pitch was ground in a hammermill and found to crush more readily than coal. About twice the percentage passing through a 200-mesh screen was obtained from pitch than from coal using the same crushing equipment. Based on the observations of these test runs, the furnace equipment manufacturer believes that petroleum pitch is a suitable fuel for a cyclone furnace and that it can be fired without difficulty, provided the minor modification to the furnace mentioned previously are made. In comparision with bituminous coal, petroleum pitch has a number of distinct advantages for use as a boiler fuel. It is much easier to pulverize, requiring lower power and maintenance costs; it requires a reduced capital cost by eliminating the requirements for fly-ash removal equipment; and it has excellent ignition and burning properties and a high BTU content.

There are many other interesting and potential uses for petroleum pitch other than that of fuel. A summary in Table IV gives properties of several pitches. Petroleum pitch as was mentioned earlier is somewhat similar to certain natural bitumens occuring in the western part of the United States. Petroleum pitch is potentially cheaper and undoubtedly could be used for many of the applications now requiring the naturally occurring bitumens. Petroleum pitch can be used satisfactorily as a binder for carbonaceous materials, although for this purpose it is not quite as good as coal tar pitch because of its higher volatile content. Another use for pitch is in beneficiation of non-coking coals when added in amounts of 10% to 20%. Various pitches have also been tested for many other lower volume uses.

PROPERTIES OF DISTILLATE PRODUCTS FROM PITCH MANUFACTURE

The economic advantage to the petroleum industry in making pitch is that of obtaining additional yields of gasoline, furnace oil, and catalytic cracking charge stock and decreased yields of No. 6 Fuel Oil.

When producing pitch by vacuum distillation, all distillate oils are straight run stocks and require further treatment only when the crude is high in nitrogen or sulfur content or when the heavy gas oil contains more metals or a higher carbon residue than is desired for catalytic cracking. Data from Baxterville Crude indicate that the entire gas oil fraction from producing a 360°F. softening point pitch is satisfactory as a catalytic cracking stock but that the furnace oil requires desulfurization to meet present day sulfur specifications.

When producing pitch by visbreaking followed by distillation, the resulting gasoline and furnace oil fractions require further treatment because of their poor stability, high sulfur content, and the low octane number of the gasoline. A large portion of the gas oil fraction can be catalytically cracked without a pretreatment, but treating the entire gas oil fraction with hydrogen greatly increases the amount of oil available for catalytic cracking. Inspections of distillate fractions from several crudes when making pitch by visbreaking followed by distillation are given in Table V. Many of these distillate fractions have been catalytically treated with hydrogen in the laboratory and all have shown considerable improvement. For example, a pretreated naphtha had a naphthene content slightly higher than that of straight run Kuwait naphtha and was shown to be a better reformer charge stock. The furnace oil fractions were easily treated with hydrogen to produce premium No. 2 Fuel Oils. The heavy gas oils, either treated or untreated, were found to be not quite as good as straight run oils for use as cracking stocks. A comparison of the the inspections and cracking characteristics of these stocks is given in Table VI.

ECONOMICS

The economics of producing solid petroleum pitch can vary widely depending upon the crude source, the refinery location and the availability of idle thermal cracking equipment. Illustrative economic studies showed a payout time after income tax of 5.6 years for making pitch from Baxterville Crude by vacuum distillation when assuming a value of $8 per ton for pitch. This value for pitch is conservative since on a BTU basis one ton of petroleum pitch (17,000 BTU per pound) is equivalent to about one and one-third tons of bituminous coal (14,000 BTU per pound). A payout time of 3.4 years was obtained for making pitch by visbreaking a vacuum reduced Eastern Venezuela Crude and then distilling the visbreaker residue. If idle thermal cracking equipment were available, this payout time would be even lower. This latter payout is quite attractive, but in each case both economics and an adequate and permanent market must be developed.

Table IV

PHYSICAL PROPERTIES OF PITCHES

Crude Source	Baxterville			Eastern Venezuela	Kuwait
Yield: % by Vol. of Crude	33.5	25.7	17.9	3.9	4.3
Inspection:					
Gravity, Solid State					
Sp. Gr., 77°/77°F.	1.103	1.099	1.153	1.124	1.196
Ring and Ball					
Softening Point: °F.	275	360	441	426	415
Penetration, ASTM D 5-49					
210°F., 100 G., 5 Sec.	23	4	2	1	---
Sediment: %					
ASTM D 473-48	---	0.07	0.13	---	1.46
Carbon Residue, Conradson: %	36.5	43.5	55.2	53.7	63.2
Proximate Analysis, Dry Basis: %					
Volatile Matter	65.5	60.8	50.9	51.8	41.0
Fixed Carbon	34.5	39.1	49.0	47.7	58.9
Ash	0.0	0.1	0.1	0.5	0.1
Analysis, Ultimate: % by Wt.					
Nitrogen	0.3	0.4	0.4	1.3	0.7
Sulfur	4.8	5.0	5.5	3.2	7.6
Hydrogen	8.6	8.8	7.8	8.6	6.6
Carbon	84.8	85.8	86.0	86.5	84.1
Undetermined	1.5	0.0	0.3	0.4	1.0
Ash as Oxide: %	---	0.08	0.11	0.52	0.14
Insoluble in Trichloroethylene: % by Wt.	0.13	0.08	0.11	0.13	---
Heating Value, BTU/Lb.	17,400	17,170	16,740	17,170	16,400
Metals: PPM					
Vanadium	114.6	141.0	186.0	841.0	348.0
Nickel	53.2	64.2	83.9	212.0	99.5
Copper	1.7	2.6	2.3	---	---
Iron	45.0	56.0	375.0	51.0	224.0

Table V

DISTILLATE OILS FROM VISBREAKING TO MAKE PITCH

Reduced Crude Charge	Baxterville	Western Venezuela	Eastern Venezuela	Kuwait
Charge Stock				
% of Crude	33.3	46.4	11.5	14.4
Softening Point: °F.	280	162	180	165
Carbon Residue: %	34.9	25.1	26.5	27.7
300°F. E.P. Gasoline				
Yield, % by Vol.	1.9	10.1	8.8	11.2
Gravity: °API	58.4	63.2	63.5	64.3
Sulfur, L: %	0.88	0.84	0.72	0.93
Research Method: Octane No.				
Clear	68.0	79.0	77.9	73.0
+3 Cc. TEL	76.2	87.2	85.6	80.3
Naphtha				
Yield, % by Vol.	2.4	6.7	5.3	6.5
Gravity: °API	44.8	44.1	44.8	44.7
Sulfur, L: %	1.17	1.34	—	1.30
Research Method: Octane No.				
Clear	49.2	60.8	55.7	51.8
+3 Cc. TEL	57.2	70.2	65.8	60.6
Characterization Factor	11.70	11.60	11.67	11.66
Furnace Oil				
Yield, % by Vol.	5.5	14.7	13.3	14.5
Gravity: °API	30.5	29.6	31.2	27.9
Sulfur, Braun-Shell: %	2.57	2.34	1.83	3.47
Aniline Point: °F.	129	118	129	114
Characterization Factor	11.50	11.39	11.52	11.25
Cracking Stock				
Yield, % by Vol.				
670°F. IBP Gas Oil	7.1	19.3	18.1	14.9
Gravity: °API	19.1	15.5	19.0	13.0
Sulfur, Braun-Shell: %	3.36	2.94	2.11	5.20
Sediment: %				
ASTM D 473-48	0.02	<0.01	<0.01	0.01
Carbon Residue, Conradson: %	0.7	1.03	1.12	1.04
Ash, Humble: %	0.0004	0.0002	0.0057	0.0004
Metals: PPM				
Vanadium	0.02	0.08	0.03	0.03
Nickel	0.08	0.05	0.07	0.05
Characterization Factor	11.53	11.33	11.55	11.05
Heavy Gas Oil				
Yield, % by Vol.	2.9	9.3	9.7	12.7
Gravity: °API	10.0	7.1	8.5	1.0
Sulfur, Braun-Shell: %	3.61	2.96	2.34	6.12
Carbon Residue, Conradson: %	14.1	13.4	16.5	16.6
Characterization Factor	11.30	11.18	11.30	10.66

Table VI

CATALYTIC CRACKING CHARACTERISTICS OF VIRGIN, CATALYTIC AND VISBREAKER GAS OILS

	Virgin Kuwait Gas Oil	Kuwait Heavy Catalytic Gas Oil	Gas Oil From Visbreaking to Make Pitch
Charge Stock Properties			
Gravity: °API	22.2	17.7	18.1
Sulfur: %	3.06	3.36	4.14
Carbon Residue: %	0.73	0.11	1.45
Vanadium, PPM	0.56	--	0.34
Characterization Factor	11.76	11.10	11.46
Conversion: % by Volume	53.8	34.2	43.3
Yields: % by Volume			
Depropanized Gasoline	49.1	25.6	35.0
Light Catalytic Gas Oil	20.7	18.7	20.4
Heavy Catalytic Gas Oil	25.5	47.1	36.3
Coke	5.2	6.6	6.6
Gasoline: Coke Ratio	9.5	3.9	5.2

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5. R. G. Goldthwait and W. R. Lehrian, U. S. Patent 2,944,958.

6. Watts, G. A. and Sage, W. L. Mechanical Engineering, Vol. 78, pp. 823-827, September, 1956.

FIGURE 1

PRODUCTION OF PITCH BY VACUUM REDUCTION

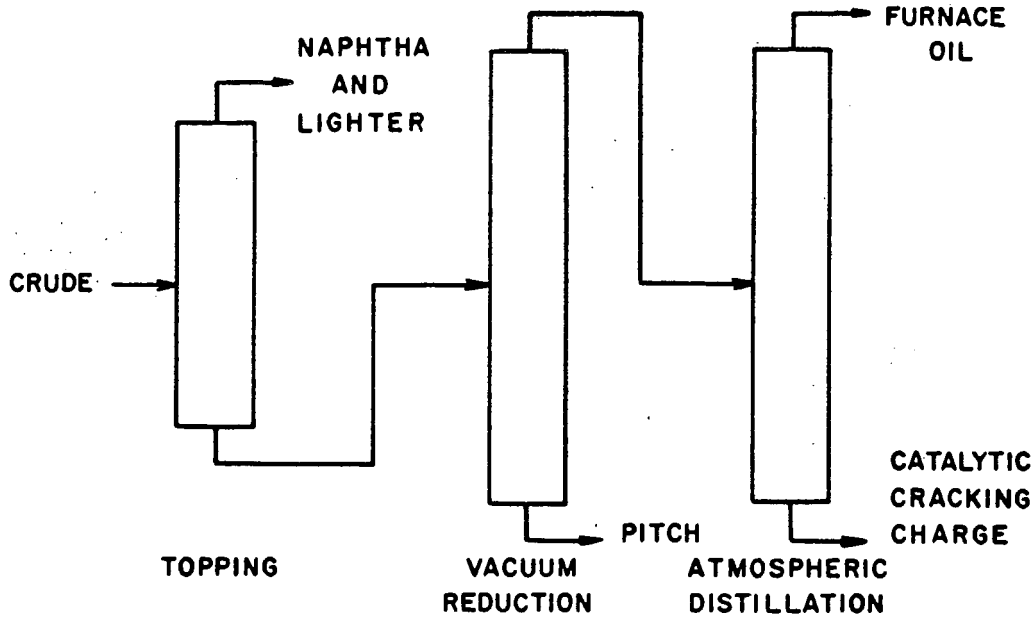
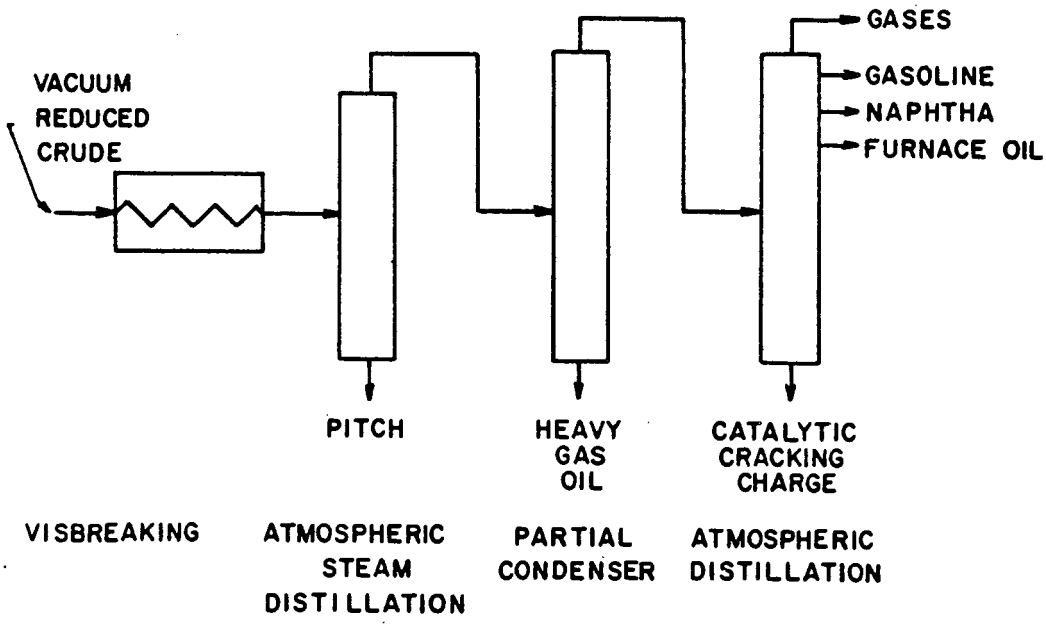


FIGURE 2

PRODUCTION OF PITCH BY VISBREAKING



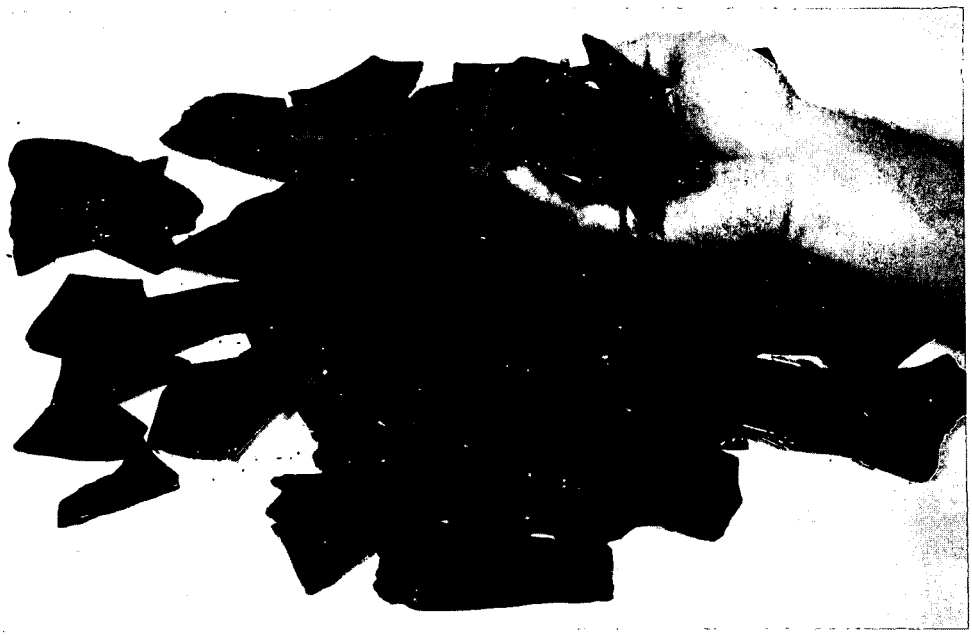


Figure 3
PETROLEUM PITCH PRODUCED BY COOLING ON A STAINLESS STEEL BELT

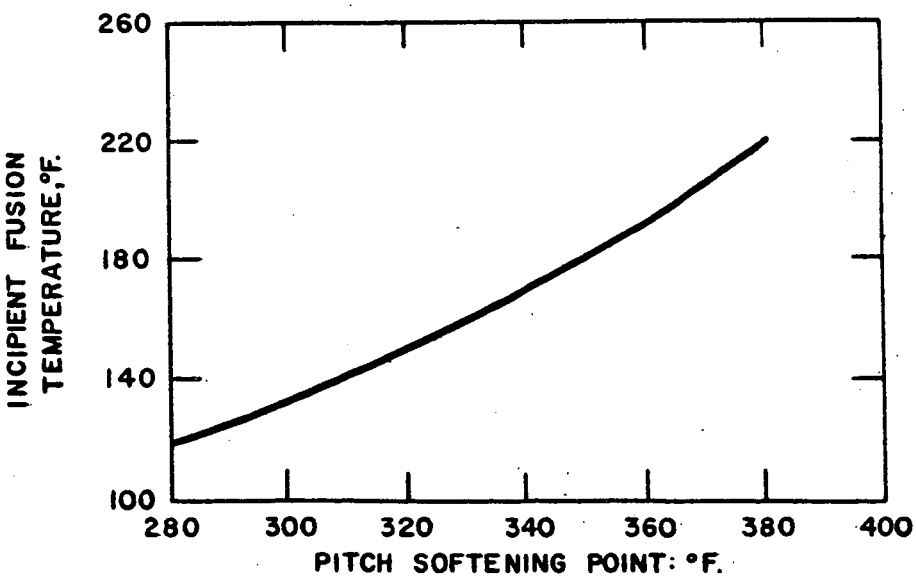



FIGURE 4
INCIPIENT FUSION POINT OF EASTERN VENEZUELA PITCH