

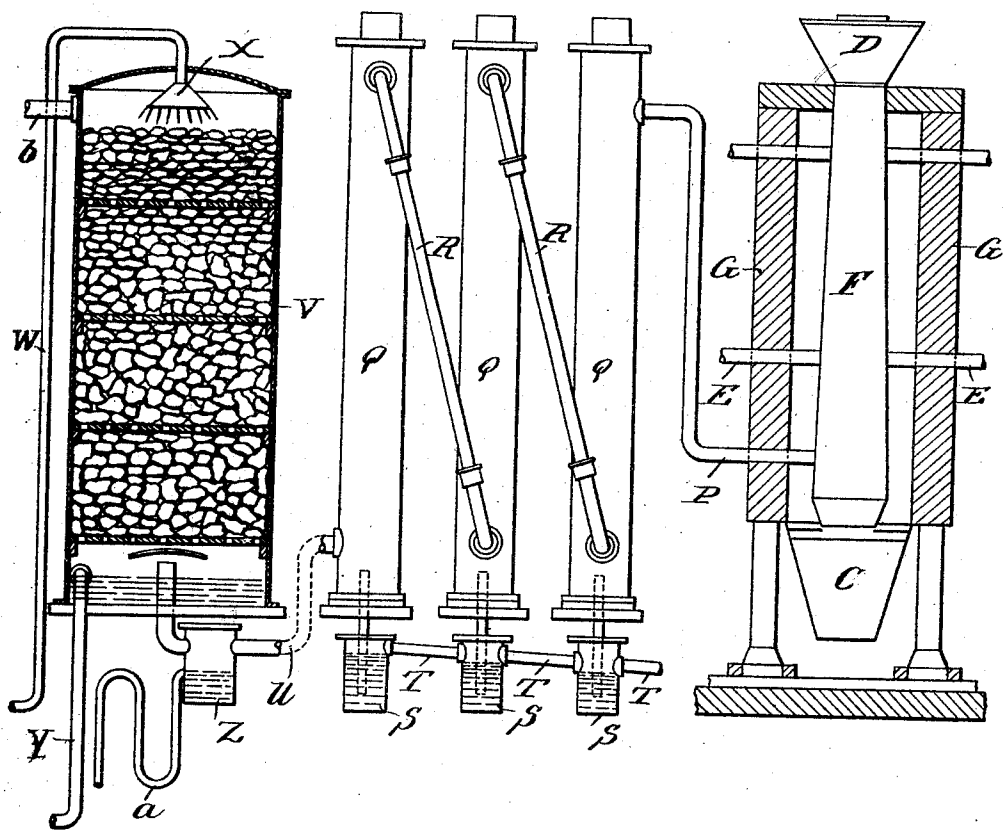
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TREATMENT AND PRODUCTION OF HYDROCARBONS

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UNITED STATES PATENT OFFICE.

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TREATMENT AND PRODUCTION OF HYDROCARBONS.

Application filed July 11, 1921. Serial No. 483,915.

(GRANTED UNDER THE PROVISIONS OF THE ACT OF MARCH 3, 1921, 41 STAT. L., 1313.)

To all whom it may concern:

Be it known that GEORGE FREDERICK FORWOOD, a subject of the King of Great Britain, residing at London, England, has invented certain new and useful Improvements in the Treatment and Production of Hydrocarbons (for which application was filed in Great Britain July 3, 1917), maturing into Patent No. 128,255.

This invention relates to the treatment of hydrocarbons of high boiling points for their conversion into hydrocarbons of lower boiling points and high hydrogen saturation, and the treatment or process is of that type in which hydrocarbon oils are vapourized and mixed with water vapour and passed over hot carbon.

According to my present invention the vapours of hydrocarbon oils and steam (in excess of the oil vapour) are passed over carbonaceous shale which remains after the volatile portions have been wholly or partially driven off from the oil bearing shale.

The quantity of steam employed depends upon the amount of moisture held by the shale at the time of distillation, the more the moisture in the shale the less excess of steam supplied from a boiler.

The spent shale is heated to a temperature varying from 450° to 600° C. as found most suitable for the particular oil to be treated; and the oil is hydrogenated, or cracked and hydrogenated simultaneously, producing a more highly saturated oil, having in most cases a lower boiling point.

The duration of the treatment depends upon the temperature employed and the rate of passage of the shale through the retort.

The process of distillation and cracking and hydrogenating may be combined. Thus a vertical retort may have the shale fed in at the top and the refuse removed from the bottom, the vapour being brought down through the refuse, instead of passing up as in Scotch practice. The lower end

of the retort is then kept at about 600° C. while the top is just hot enough (about 400° C.) to liberate the oil vapour. Steam is then admitted either at the top so as to pass through the fresh and distilling shale to carry off the vapour, or it is admitted lower so that the mixed vapours pass down through the hot spent shale, which is mineral mixed with finely divided carbon. Thus by this invention I distil the shale, crack the produced shale oil and hydrogenate it as follows:—

1. Distillation of the shale at the top of the retort.

2. Cracking of the shale oil lower down the retort.

3. Hydrogenation of the cracked shale oil at the lower end of the retort by saturating it with hydrogen produced by the decomposition of steam admitted by means of the carbon in the spent shale.

And further I cause the cracking (or disassociation) of the oil in the presence of steam and the carbon of the spent shale and use the hydrogen produced by the decomposition of the steam in the hydrogenation of the cracked oil.

In carrying out the method of procedure in simple hydrogenation, a retort, or retorts, either horizontal or vertical or inclined at a suitable angle, is filled with spent shale and the spent shale is heated to a temperature varying from 450° to 600° C. Steam preferably superheated and low boiling oil of say a maximum boiling point about 150° C., in the proportions of one volume of oil to about 4.7 volumes of water, are passed through the heated carbonaceous shale. The steam is decomposed during its passage through the heated carbonaceous or spent shale and the hydrogen produced is utilized to hydrogenate or saturate any unsaturated bodies present in the oil. When employing a vertical retort, of any known type, for the purpose, the steam and oil may be admitted to the top of the retort and the products—

oil, excess steam and gas removed by a pipe at the bottom of the retort, or the steam and oil may be admitted at the bottom of the retort and the products,—oil, excess steam and gas removed by a pipe at the top of the retort.

The oil, excess steam and gas are conveyed from the retort to condensers where the steam and the bulk of the oil is condensed, the gas, which still holds some very light oil vapours, is scrubbed or washed with heavy oil which removes these light oil vapours, when saturated with light oil vapours this heavy wash-oil can be distilled, preferably with steam, in order that it may yield the light oil.

A door is provided in both the horizontal, vertical and the inclined retort, so that the mineral matter, left after the carbon has been used by the steam, may be removed from time to time and replaced by fresh carbonaceous shale.

The scrubbed permanent gas may be used to heat the retort or retorts.

Example.

A vertical retort 18 inches high and 2 inches in diameter, holding about two pounds of spent shale broken to the size of about 1/4 inch cube was heated to a temperature of 550°–600° C. Crude shale spirit having a maximum boiling point of 150° C. together with superheated steam was passed upwards through the heated carbonaceous shale. The proportion of shale spirit and water used to generate the steam was one volume of the former to two and three-quarters volumes of the latter. The duration of the treatment was at the rate of 700 cubic centimetres of shale per hour. The oil, permanent gas, and excess steam, that is, the steam not converted into permanent gas, were passed from the top of the retort into a water-cooled condenser and the condensed water and oil passed into a receiver while the permanent gas carrying light spirit vapours was passed through a scrubber, filled with broken steatite, (broken firebrick, scrap iron, wooden boards laid crosswise will do equally well, the idea being to present a large scrubbing surface), down which flowed heavy shale oil distilling between 250° and 400° C. The permanent gas carrying the light shale spirit vapours passed through the scrubber in the opposite direction.

The scrubber oil, containing the light shale spirit was afterwards distilled with steam and the resultant light spirit in volume about 4 per cent of the total oil passed through the retort, was added to the condensed oil collected in the receiver. The whole of this light spirit was subjected to a distillation and washing treatment for final refining, and the product was petrol or motor-spirit.

A comparison of the boiling points and analysis of the shale spirit before and after hydrogenation is given below:—

Oil before hydrogenation. Begun to distil at 63° C.		Oil after hydrogenation. Begun to distil at 18° C.	
Distilling below—	Volume, per cent.	Distilling below—	Volume, per cent.
100° C.-----	7.0	100° C.-----	20.5
110° C.-----	17.0	110° C.-----	39.0
120° C.-----	37.0	120° C.-----	55.5
130° C.-----	64.5	130° C.-----	77.5
140° C.-----	82.0	140° C.-----	89.5
150° C.-----	100.0	150° C.-----	100.0
Hydrocarbons.		Hydrocarbons.	
Unsaturated.....	62	Unsaturated.....	17
Aromatic.....	27	Aromatic.....	47
Paraffin.....	11	Paraffin.....	26

In carrying out the method of procedure in combined cracking and hydrogenation, the apparatus used and the method of procedure is similar to that employed in simple hydrogenation, hereinbefore described.

Example A.

A vertical retort about 18 inches high and 2 inches in diameter, holding about two pounds of spent shale, broken to the size of about 1/4 inch cube, was heated to a temperature of about 600° C.

Crude shale oil, boiling between 150° and 180° C. together with superheated steam was passed upwards through the heated carbonaceous shale.

The proportion of shale oil and water used to generate the steam was one volume of the former to one and three-quarters volumes of the latter. The duration of the treatment was at the rate of 425 cubic centimetres of shale oil per hour. The oil, permanent gas and excess steam, that is, the steam not converted into permanent gas, were passed from the top of the retort into a water-cooled condenser and the condensed water and oil passed into a receiver while the permanent gas carrying light spirit vapours was passed through a scrubber, filled with broken steatite (although broken fire-brick, scrap iron, wooden boards laid crosswise, will be equally well), down which flowed heavy shale oil distilling between 250° and 400° C. The permanent gas carrying the light shale spirit vapours, produced by the cracking and hydrogenation of the original shale oil used, passed through the scrubber in the opposite direction. The scrubber oil containing the light shale spirit was afterwards distilled with steam and the resultant light spirit, in volume about 4 3/4 per cent of the total oil passed through the retort, was added to the condensed oil collected in the receiver. The whole of this

light spirit was subjected to a distillation and washing treatment for final refining, and the product was petrol or motor-spirit.

A comparison of the boiling points and analysis of the shale oil before and after hydrogenation is given below:—

Oil before hydrogenation. Began to distil at 150° C.		Oil after hydrogenation. Began to distil at 32° C.	
Distilling below—	Volume, per cent.	Distilling below—	Volume, per cent.
150° C.....	None.	100° C.....	5.0
		110° C.....	8.0
		120° C.....	10.0
		130° C.....	30.0
		140° C.....	60.0
		150° C.....	96.0
		Above 150° C.....	4.0
180° C.....	100.0		
Hydrocarbons.	Volume, per cent.	Hydrocarbons.	Volume, per cent.
Unsaturated.....	69	Unsaturated.....	24
Aromatic.....	21	Aromatic.....	38
Paraffin.....	10	Paraffin.....	38

Example B.

A vertical retort about 18 inches high and two inches in diameter, holding about two pounds of spent shale, broken to the size of about ¼ inch cube, was heated to a temperature of about 600° C.

Crude shale oil, boiling between 180° and 220° C. together with superheated steam was passed upwards through the heated carbonaceous shale.

The proportion of shale oil and water used to generate the steam was one volume of the former to two volumes of the latter. The duration of the treatment was at the rate of 790 cubic centimetres of shale oil per hour. The oil, permanent gas and excess steam, that is, the steam not converted into permanent gas, were passed from the top of the retort into a water-cooled condenser and the condensed water and oil passed into a receiver while the permanent gas carrying light spirit vapours was passed through a scrubber, filled with broken steatite (although broken fire-brick, scrap iron, wooden boards laid crosswise will do equally well) down which flowed heavy shale oil distilling between 250° and 400° C. The permanent gas carrying the light spirit vapours, produced by the cracking and hydrogenation of the original shale oil used, passed through the scrubber in the opposite direction. The scrubber oil containing the light shale spirit was afterwards distilled with steam and the resultant light spirit, in volume about 4 per cent of the total oil passed through the retort, was added to the condensed oil collected in the receiver. The whole of this light spirit was subjected to a distillation and washing treatment for final refining, and the product was petrol or motor-spirit.

A comparison of the boiling points and analysis of the shale oil before and after hydrogenation, is given below:—

Oil before hydrogenation. Began to distil at 180° C.		Oil after hydrogenation. Began to distil at 32° C.	
Distilling below—	Volume, per cent.	Distilling below—	Volume, per cent.
180° C.....	None.	100° C.....	4.0
		110° C.....	8.5
		120° C.....	12.5
		130° C.....	32.5
		140° C.....	56.5
		150° C.....	87.5
		Above 150° C.....	12.5
220° C.....	100.0		
Hydrocarbons.	Volume, per cent.	Hydrocarbons.	Volume, per cent.
Unsaturated.....	60	Unsaturated.....	10
Aromatic.....	11	Aromatic.....	14
Paraffin.....	29	Paraffin.....	76

In carrying out the method of procedure in the combined distillation of shale and the cracking and hydrogenation of the product, a vertical retort, or retorts, is filled with shale broken to a convenient size and preferably air dried since many freshly mined shales, especially the Kimmeridge shales, contain large quantities of uncombined water or moisture amounting in some cases to ten per cent. The retort or retorts, employed may be of any known type constructed wholly of fireclay or partly of iron or partly of fireclay as found most suitable. The retort, or retorts, is fitted with a charging door at the top for feeding the retort with fresh shale and with a discharging door at the bottom for discharging the spent shale continuously or at intervals. Near the bottom of the retort is a pipe for conveying the products away.

The retort, or retorts, is set in a furnace and heated by means of the spent shale, or by the gaseous products conveyed away from the retort, or partly by the spent shale and partly by the gaseous products.

The upper part of the retort is heated to about 400° C. and the lower part to about 600° C. At a point near the top of the retort or lower down a pipe or pipes is fixed to convey steam, preferably superheated to the interior of the retort. The steam pipe should not be in direct contact with the fire in the furnace or combustion chamber or it will soon be burned away but it may be set in the hot brickwork of the setting to assist in keeping the steam dry.

By heating the lower part of the retort at about the temperatures stated I decompose the steam to carbon monoxide and hydrogen by means of the carbon in the spent shale.

If the gases are practically free from carbon monoxide it is evident that the steam is not decomposed and therefore there is no

hydrogen available for hydrogenation, a feature necessary in my process and not provided for in known apparatus consisting of a vertical retort to which shale and steam are supplied at the top.

When the retort is filled with shale and is in working order the fully spent shale will occupy the lower portion of the retort, the partly spent shale at the middle portion and the freshly distilling shale at the top of the retort. Steam generated from the freshly distilling shale together with oily vapours are given off at the top portion of the retort, here they meet with steam generated in a boiler and conveyed to the interior of the retort by means of the pipe hereinbefore mentioned and together the steam and oil vapours pass downwards to the hotter zone of the retort where the oil is cracked and the steam is decomposed, and the hydrogen produced by the decomposition of the steam is used to hydrogenate the unsaturated bodies contained in the shale oil.

The products of the distillation of the shale, the cracking and hydrogenation of the resultant shale oil, the permanent gas and excess steam are then conveyed away by the pipe provided near the bottom of the retort to a condenser or condensers and the condensed oil and water are conveyed to a receiver or receivers. The uncondensed portion, or gas is scrubbed or washed with heavy oil to remove light oil vapours after which the permanent gas may be utilized to heat the retort furnace or for other purposes.

Example.

A vertical iron retort, set in a furnace, and fitted with a charging door at the top, discharging door at the bottom, outlet pipe for products near the bottom and steam pipe near the top, was charged with a few pounds of air dry fresh shale crushed to a suitable size. The temperature of the retort near the top was about 420° C. and when the temperature of the spent shale near the bottom of the retort had risen to about 580° C., dry steam was admitted to the retort through the pipe provided for the purpose.

From time to time a little of the spent shale was discharged from the bottom door and a little fresh shale was admitted to the retort through the top door.

The products of the distillation of the shale, the cracking and hydrogenating of the resultant shale oil, the permanent gas containing light shale oil vapours and the excess steam were conveyed away, by the pipe, near the bottom of the retort, provided for the purpose, to a condenser and the condensable portion of the products, oil and water, were collected in a receiver where the oil and water were separated by reason of their different densities. The uncondensable

gas carrying light oil vapours was then passed upwards through a scrubber filled with broken steatite (although firebrick, scrap iron, wooden boards laid crosswise, will do equally well).

Heavy shale oil distilling between 250° and 400° C. flowed from the top of the scrubber downwards, and in the opposite direction to the flow of the gas. In this manner the gas was freed from the light oil vapours. The scrubber oil, containing the light shale spirit, was afterwards distilled with steam and the resultant light spirit, in volume about four per cent of the total oil yielded from the shale, was added to the condensed oil collected in the receiver. The whole of the oil was subjected to a distillation for the purpose of obtaining data respecting the boiling points. The duration of the treatment was at the average rate of half a pound of shale per hour. The proportion of water, used to generate the steam, and shale was roughly one-third of a pound of water to one pound of shale.

A comparison of the boiling points and analysis of the shale oil (a) produced during an ordinary retorting of the shale in the vertical retort at a temperature of about 420°-450° C., and (b) that produced during the retorting of the shale in the upper part of the vertical retort at a temperature of about 420° C. and a subsequent cracking and hydrogenating of the resultant shale oil in the lower part of the retort at a temperature of about 580°-600° C. is given below:—

(a) Shale oil produced during an ordinary retorting of the shale at about 420°-450° C.		(b) Oil produced during the retorting of the shale at about 420° C., and subsequent cracking and hydrogenating at about 580°-600° C.	
Began to distil at 70° C.		Began to distil at 38° C.	
Distilling below—	Volume, per cent.	Distilling below—	Volume, per cent.
100° C.-----	1.0	100° C.-----	18.0
110° C.-----	1.5	110° C.-----	29.5
120° C.-----	2.0	120° C.-----	39.5
130° C.-----	2.5	130° C.-----	53.0
140° C.-----	3.0	140° C.-----	71.0
150° C.-----	3.5	150° C.-----	86.0
160° C.-----	4.0	160° C.-----	91.0
170° C.-----	9.5	170° C.-----	93.0
180° C.-----	13.5	180° C.-----	95.0
190° C.-----	19.0	190° C.-----	97.5
200° C.-----	23.0	200° C.-----	99.0
210° C.-----	27.0	Above 200° (pitch)-----	1.0
220° C.-----	27.5		
230° C.-----	30.0		
240° C.-----	32.0		
250° C.-----	35.0		
260° C.-----	39.0		
270° C.-----	42.0		
280° C.-----	46.0		
290° C.-----	50.0		
300° C.-----	54.0		
310° C.-----	61.0		
320° C.-----	64.0		
330° C.-----	66.0		
340° C.-----	67.0		
350° C.-----	76.5		

NOTE.—The residue of 23.5 per cent distilling above 350° C. was pitch.

(a) Shale oil produced during an ordinary retorting of the shale at about 420°-450° C.		(b) Oil produced during the retorting of the shale at about 420° C., and subsequent cracking and hydrogenating at about 580°-600° C.	
Hydrocarbons.	Volume, per cent.	Hydrocarbons.	Volume, per cent.
Unsaturated.....	66	Unsaturated.....	9
Aromatic.....	12	Aromatic.....	40
Paraffin.....	22	Paraffin.....	51

The foregoing process is not in the least limited to any particular apparatus, but for the purpose of illustration the drawing illustrates a sectional elevation of an apparatus suitable for carrying out the improved process or method.

The drawings show diagrammatically one arrangement of parts suited to the carrying out of my process.

Between the walls G of a furnace or heater a vertical retort F may be placed having an inlet hopper D at the top and a spent shale hopper C at the base, the retort F being supplied with steam pipes E at any required position along its length and also with an outlet pipe P near its bottom and leading to condensers Q.

The shale is fed into the retort F through the hopper D and when the retort is filled the hopper is closed. The retort is heated by the products of combustion from the fuel in the lower part of the furnace and the greatest heat is imparted to the lower part of the retort but the retort may be heated by producer or other gas or the flames thereof.

The spent shale in the lower part of the retort falls into the hopper C and can be removed at intervals and the retort may at the same time be replenished by raw shale.

Steam is admitted by the pipes E and pass with the vapours through the fresh and distilling shale at the middle and upper part of the retort and then through the hotter spent shale by the pipe P to a plurality of condensers Q and may be collected either by water or atmospherically. The gases passing from one condenser to another through the medium of pipes R as usual and are condensed and the oil from the condensed gas and vapours is collected in the receivers S from which it is taken by a pipe T to an oil tank not shown, the uncondensed vapours passing by way of a pipe U to a scrubber V.

This scrubber is filled with broken brick, coke or boards laid crosswise and heavy oil is supplied to the scrubber from a suitable pump not shown, by the pipe W and is sprayed over the broken coke or brick by a sprayer X and after passing through the broken brick or coke, flows to a storage tank by way of the outlet pipe Y.

Any oil from the uncondensed gases and vapours passed to the scrubber V from the pipe U is collected in the receiver Z and passes to a tank by the seal pipe a the finished gas passing away by the scrubber V by the pipe b.

What I do claim as my invention and desire to secure by Letters Patent is:—

1. The process of treating hydrocarbon-containing shale consisting of heating a retort, filled with shale, to about 400° C. at the upper part and to about 600° C. at the lower part, conveying steam to the interior of the retort, passing the oil distilled from the shale at the upper portion of the retort together with the steam downwardly through the partially spent shale to crack said oil and then through the spent shale at the lower part of the retort to decompose the steam by means of the carbon in the spent shale and thereby produce hydrogen, using said hydrogen to hydrogenate the unsaturated bodies contained in the shale oil, and drawing away the products from the lower end of the retort.

2. The process of treating hydrocarbon-containing shale comprising heating a column of finely divided shale to about 400° C. at its upper portion and to about 600° C. at its lower portion, admitting steam to the upper portion of said column, passing the oil distilled from said upper portion of said column together with said steam through said column to crack said oil and to decompose said steam to produce hydrogen, and hydrogenating the unsaturated bodies contained in the distilled oil by means of such hydrogen.

In testimony whereof I have hereunto set my hand in presence of two subscribing witnesses.

GEORGE FREDERICK FORWOOD.

Witnesses:

H. E. WRIGHT,
H. MAYKELS.