

March 24, 1964

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3,126,330

JET FUEL PRODUCTION

Filed April 6, 1959

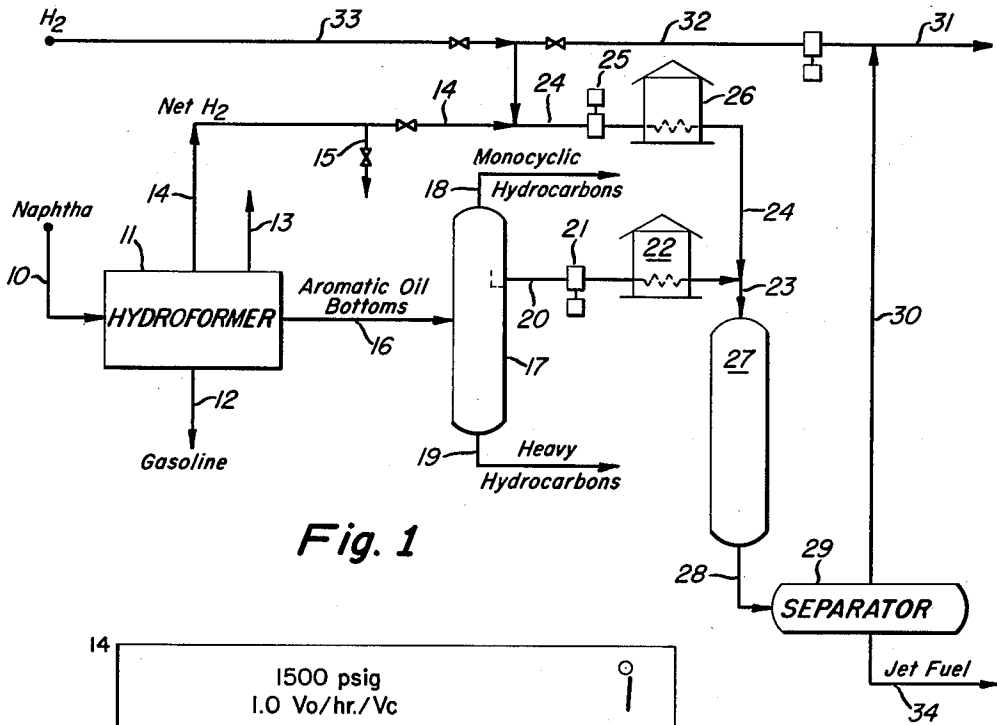


Fig. 1

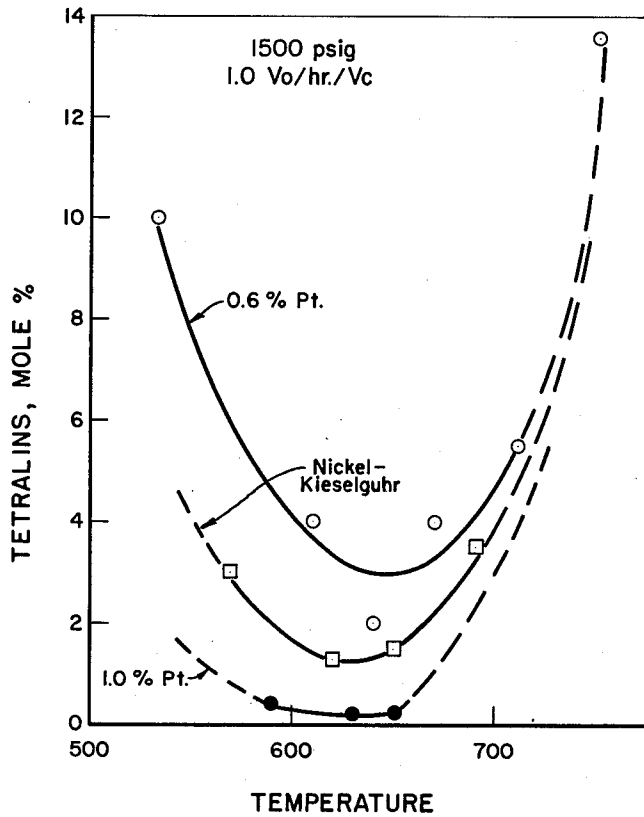


Fig. 2

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JET FUEL PRODUCTION

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Filed Apr. 6, 1959, Ser. No. 804,437
3 Claims. (Cl. 208-15)

This invention relates to the production of a high-performance jet fuel of the type required by supersonic aircraft or ballistic missiles, which fuel is characterized by high temperature stability, maximum energy content, and good handling characteristics at both high and low temperatures.

Fuels for supersonic jet engines should have a net heat of combustions upwards of about 18,400 B.t.u. per pound and at least about 130,000 B.t.u. per gallon, an aromatics content of less than 2 percent and preferably less than 1 percent, a freezing point below -40° F., good high temperature stability, and low viscosity at -30° F. Stability at high temperatures, in the region of about 800° F., is necessary in order to permit use of the fuel prior to combustion as a coolant for the engine and air frame. The object of this invention is to provide a high-performance jet fuel which will meet these requirements, and to do so by a technique which will not require excessive capital investment and operating expense. Other objects will be apparent from the following detailed description.

When naphthas having an end point in the range of about 380 to 440° F. are hydroformed with a platinum-alumina catalyst, an aromatic oil is produced which is higher boiling than naphtha and which is sometimes referred to as "polymer" or "bottoms." The high-performance jet fuel is obtained by hydrogenating the fraction of said aromatic oil which boils in the range of about 450 to 570° F. to obtain substantially complete saturation thereof. The initial boiling point of the aromatic oil should be above the end point of the naphtha which was originally hydroformed and it should be high enough to substantially eliminate monocyclic aromatic hydrocarbons although a small amount of the latter may be tolerated. Said fraction should not include components higher boiling than about 570° F. because such higher boiling materials have been found to deactivate the catalyst employed in the hydrogenation step. In addition, feed components higher boiling than about 570° F. will raise the freezing point and increase the viscosity of the product fuel. The aromatic oil obtained as a by-product of naphtha hydroforming with platinum-on-alumina catalyst, as hereinabove described, requires no desulfurization, extraction or other expensive treatments heretofore deemed necessary for obtaining jet fuels of desired quality.

The invention will be more clearly understood from the following detailed description of a specific example read in conjunction with the accompanying drawings which form a part of the specification and in which

FIGURE 1 is a schematic flow diagram illustrating our operating technique, and

FIGURE 2 is a chart showing the effects of time and temperature in obtaining substantially complete product saturation, i.e., of minimizing aromatics and tetralins.

The naphtha is introduced by line 10 to hydroformer 11 which should be of the platinum-on-alumina type but

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which may be either regenerative or non-regenerative and which is conventionally operated at temperatures in the range of about 850 to 1000° F. and pressures in the range of 150 to 750 p.s.i. and at volume hourly space velocities in the range of 0.5 to 5 , examples of such platinum-on-alumina hydroforming processes being Platforming, Ultraforming, Houdriforming, Catforming, etc. It is essential that the naphtha charge have an end point of at least 360° F. and preferably in the range of 380 to 440° F. in order to obtain an aromatic oil by-product which is higher boiling than hydroformed naphtha. Usually the naphtha charged to the hydroformer is hydrofined, for example, with a catalyst comprising cobalt and molybdenum oxides on alumina in order to reduce the sulfur content of the naphtha down to about 5 or 10 p.p.m. before said naphtha is hydroformed. The main product of hydroforming is the motor fuel or gasoline fraction withdrawn through line 12. A hydrocarbon gas fraction may be withdrawn through line 13. Net hydrogen is withdrawn through line 14 and may be used for the hydrofining, vented from the system or charged to a purifier through line 15.

An "aromatic oil," sometimes called "polymer" or "bottoms," is withdrawn from the hydroformer product fractionation through line 16 and is separated in fractionator 17 into a monocyclic hydrocarbon fraction withdrawn overhead through line 18, a high boiling or heavy hydrocarbon fraction withdrawn as bottoms through line 19 and a heart cut boiling in the range of about 450 to 570° F. withdrawn through line 20. It should be understood that any known fractionating technique may be employed and that the fraction boiling in the range of 450 - 570° F. may be sent to intermediate storage.

Oil from line 20 is introduced by pump 21 through heater 22 and transfer line 23 together with about 1000 to $10,000$, and preferably about 5000 to 7000 s.c.f., of a hydrogen-rich gas containing about 85% or more of hydrogen introduced from line 24 by compressor 25 through heater 26 to hydrogenation vessel 27 which in this example is operated at about 620° F. under a pressure of about 1500 p.s.i. with a space velocity of about 0.5 volume of aromatic oil per hour per volume of platinum-on-alumina catalyst containing about 1 percent platinum. The hydrogenated product is then passed by line 28 to separator 29 from which hydrogen may be withdrawn through line 30 and either discarded through line 31 or recycled through line 32. Purified hydrogen or hydrogen from an extraneous source may be introduced by line 33. The product withdrawn from separator 29 may require subsequent fractionation so that it will have an initial boiling point not substantially lower than 400° F. although in many cases it is suitable directly for use as high quality jet fuel.

The hydroformer 11 in the foregoing example is preferably an Ultraformer as described by Forrester, Conn and Malloy in Petroleum Refiner, volume 33, No. 4, page 153 (1954), and in U.S. Patent 2,773,008. The catalyst employed in hydrogenation vessel 27 is preferably a platinum-on-alumina catalyst prepared as described in Coley et al. patent application Serial No. 610,378, filed September 17, 1956, now United States Letters Patent No. 2,911,375, although other types of platinum-on-alumina catalyst may be employed and other highly active hydrogenation catalysts may be used such, for example, as 55 percent nickel-on-kieselguhr.

The conditions employed in hydrogenation reactor 27 must be effective for obtaining substantially complete saturation. When a bicyclic aromatic such as naphthalene is hydrogenated, the reaction occurs in two steps: the conversion from naphthalene to tetralin is fast but the subsequent conversion from tetralin to decalin is relatively slow. For obtaining substantially complete saturation, the amount of tetralin left in the product should be reduced to a minimum. From FIGURE 2 it will be noted that 1 percent platinum-on-alumina catalyst is more effective than nickel-on-kieselguhr which in turn was more effective than the 0.6 percent platinum-on-alumina. All of these catalysts were most effective at temperatures in the range of 550 to 700 and preferably about 600 to 680 or about 630° F. when the pressure is 1500 p.s.i. and the space velocity is 1. With the nickel-on-kieselguhr catalyst and the 0.6 percent platinum catalyst, a lower space velocity must be employed in order to obtain the substantially complete saturation effected by the 1 percent platinum catalyst.

The hydrogenated hydroformer heart cut was found to contain about 94 percent bicyclic and 6 percent monocyclic naphthenes, the bicyclic naphthenes containing about 11 to 13 carbon atoms per molecule. It contained no paraffins. When the aromatic oil heart cut was hydrogenated, it consumed 3,700 standard cubic feet of hydrogen per barrel of aromatic oil. This large hydrogen input gave a product yield of 116 volume percent.

Bicyclic naphthenes are present in crude oil, but the desired types are not readily separated from other hydrocarbons of similar boiling range. The corresponding bicyclic aromatics are abundant in cycle gas oil, i.e., the refractory gas oil separated from product gasoline when gas oil was catalytically cracked. However, cycle gas oils usually contain large amounts of undesirable paraffins and monocyclic naphthenes and aromatics. A feed for subsequent hydrogenation enriched in the desired bicyclic aromatics can be obtained from the cycle oil by extraction. The cycle oil extract will still contain some of the undesirable compounds, the amount of which will vary with the nature of the solvent and the conditions employed for effecting extraction.

When a cycle gas oil was extracted and then hydrogenated to effect saturation, a product was obtained which has 6% paraffins, 38% monocyclic, 1% tricyclic, and 55% bicyclic naphthenes. The bicyclic naphthenes may be concentrated by eliminating the higher boiling portion of the product by distillation.

A product rich in the desired bicyclic naphthenes can be obtained from the cycle oil by employing fractionation procedures instead of extraction. Narrow boiling cuts, of as high as about 60° F. boiling range, preferably 30–40° F. boiling range, are obtained from a cycle oil which boils in the range of 450–570° F. The narrow boiling cuts are then hydrogenated. The lower boiling portion of the hydrogenated product which contains the desired bicyclic naphthenes is separated from the total product by distillation. When a 540–570° F. fraction of the cycle oil was hydrogenated, the total product contained 28% monocyclic naphthenes, 6% tricyclic naphthenes, 31% paraffins, and only 35% bicyclic naphthenes. After eliminating the higher boiling 60% of the product by distillation, the remaining lower boiling portion was substantially 100% naphthenic in composition and consisted of about 20% mono-, 70% bi-, and 10% tricyclic naphthenes. The higher boiling 60% of the hydrogenated gas oil product contained only 10 mol percent of bicyclic naphthenes and, because of its paraffinic nature, would be more suitable for distillate fuels.

In Table I we have set forth the gravity, distillation range, weight percent sulfur, weight percent hydrogen and volume percent aromatics when hydrogenating hydroformer bottoms as compared with hydrogenating a cycle oil fraction or a cycle oil extract, the cycle oil fraction and

extract, respectively, having been pretreated by hydrodesulfurization.

TABLE I
Hydrogenation of Bicyclic Aromatics

	Reformer Bottoms		Cycle-Oil Fraction		Cycle-Oil Extract	
	Feed	Product	Pretreated Feed	Product	Pretreated Feed	Product
Gravity, ° API.....	10.4	31.4	36.3	38.8	29.4	37.3
ASTM Distillation, ° F.:						
Initial.....	455	391	504	443	362	364
10%.....	461	401	504	484	403	388
50%.....	474	409	534	522	441	424
90%.....	502	430	549	545	467	468
Max.....	518	472	570	550	490	488
Sulfur, Wt. Percent.....	.0004	.0003	.003	.002	.03	-----
Hydrogen, Wt. Percent.....	7.86	13.32	13.46	14.06	11.90	13.74
Aromatics, Vol. Percent.....	100	.05	20.5	<2	53	0.5

In Table II we have shown the jet fuel properties of the hydrogenated products.

TABLE II
Properties of Hydrogenated Products

	Suggested Properties	Product from—		
		Reformer Bottoms	Cycle-Oil Fraction*	Cycle-Oil Extract
Heat of Combustion:				
Net b.t.u./lb.....	18,400 Min.....	18,450	18,450	18,500
Net b.t.u./gal.....	-----	134,000	134,000	130,000
Smoke Point, mm.....	-----	21	20	25
Aromatics, Vol. percent.....	5 Max.....	0.5	<1.5	0.5
Thermal Stability:				
Preheater, Color Code.....	3 Max.....	3	-----	-----
Pressure Drop, Inches Hg.....	1 Max.....	0.2	-----	-----
ASTM Initial Boiling Point, ° F.....	400 Min.....	391	443	364
Freezing Point, ° F.....	−40 Max.....	−110	−70	−70
Viscosity, cs. at −30° F.....	low.....	12.6	35.3	12.3

* 0–40% fraction of hydrogenated cycle oil, Table I.

From the foregoing table, it will be noted that we have produced a jet fuel from the reformer bottoms having a net B.t.u. per pound of about 18,450 and a net B.t.u. per gallon of about 134,000, which jet fuel has a freezing point below −100° F., namely about −110° F., which has a low viscosity, namely a viscosity of only 12.6 centistokes at −30° F., which is thermally stable and which has a smoke point of 21 millimeters. The corresponding products obtained from cycle gas oil have a somewhat higher freezing point and although they were comparable in quality, they required further processing steps such as the hydrogenating or hydrodesulfurizing and extraction and/or distillation. In Table II, heat of combustion was calculated from hydrogen content (Ind. Eng. Chem., volume 43, page 981), which in turn was obtained in the manner described in Anal. Chem., volume 28, page 324. The freezing point was determined by ASTM designation D1477–57T. The viscosity was determined by the tentative method of test for kinematic viscosity, designation D445–53T, ASTM standards on petroleum products and lubricants November 1957. The smoke point was determined by ASTM designation D1322–54T. The thermal stability was determined in the CFR Fuel Coker (American Society of Testing Materials, Appendix XXV, Proposed Method Test of Thermal Stability of Aviation Turbo Fuels) except that the procedure was modified in that a one quart sample was recirculated for 5 hours with a temperature of 450° F. in the preheater and 500° F. in the filter. The stability test is very severe as jet fuels which pass present specifications would fail in a few minutes in this test. The volumetric heating value of the jet fuels herein-

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above described give more than 5 percent more energy than prior fuels of similar volatility. Volatilities of the jet fuels could, of course, be decreased if desired by distilling off the lower boiling components. These remarkable, high performance jet fuels can easily be made from petroleum by simply hydrogenating the defined heart cut of hydroformer bottoms and the hydrogen produced by the hydroforming itself may in many cases be adequate to provide the required hydrogen for the jet fuel production.

We claim:

1. The method of making a thermally stable highly decalinic hydrocarbon jet fuel having at least about 133,000 B.t.u. per gallon, at least about 18,400 B.t.u. per pound, an aromatic content not substantially higher than about 0.5 volume percent, and a freezing point in the vicinity of -100° F. and having a viscosity at -30° F. of approximately 12 to 15 centistokes, which method comprises hydroforming a naphtha having an end point in the range of about 380 to 440° F. with a platinum-on-alumina catalyst at a pressure in the range of about 150 to 750 p.s.i. and at a temperature in the range of about 850 to 1000° F. to produce a hydroformed naphtha and a higher boiling aromatic oil, distilling the aromatic oil

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to obtain a fraction boiling in the range of about 450 to 570° F. and hydrogenating said fraction in the presence of an active hydrogenation catalyst to obtain said jet fuel by substantially complete saturation of said fraction.

2. The method of claim 1 wherein the hydrogenation catalyst is platinum-on-alumina and contains about .5 to 2 weight percent platinum.

3. A thermally stable highly decalinic hydrocarbon jet fuel having a heat of combustion of about 18,400 B.t.u. per pound and 134,000 B.t.u. per gallon, an aromatics content not substantially higher than about 0.5 volume percent, having a freezing point in the vicinity of -100° F. and having a viscosity at -30° F. of approximately 12 to 15 centistokes.

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