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3,000,815

**PROCESS FOR THE HYDROGENATION OF A
KEROSENE TYPE FUEL**

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No Drawing. Filed Oct. 22, 1959, Ser. No. 847,903
2 Claims. (Cl. 208—144)

My invention pertains to a process for improving the burning qualities of a kerosene type fuel when burned in a gas turbine. More particularly, my invention pertains to a process including catalytic hydrogenation of a kerosene type gas turbine fuel so as to improve its luminosity number.

One of the problems encountered in the employment of gas turbine fuels is their tendency to form carbon upon combustion. The carbon thus formed creates noxious exhaust smoke which is highly undesirable. The combustion-formed carbon is also deposited inside the combustor where it interferes with the operation of the spark and the fuel atomizing nozzle, and also contributes to the warping of the combustion chamber by causing uneven heating.

The tendency of a fuel to form carbon when burned in a gas turbine engine decreases with a decreasing C/H ratio. This is in accord with previously known data showing a greater carbon deposition for aromatics than paraffins and an increase in carbon deposition with an increase in boiling point of the fuel. Unfortunately, a substantial percentage of the kerosene fraction produced according to modern petroleum processing methods is composed of aromatics. Thus, to meet the rising standards set for gas turbine fuels, conversion or removal of a portion of the aromatics contained in kerosene is indicated.

A standard indicative of the carbon-forming tendency of a fuel is its luminosity number. As this standard is more directly related to the burning qualities desired in a gas turbine fuel than is maximum allowable aromatic content, it is anticipated that such standard will be incorporated into gas turbine fuel specifications in the near future. One commercial jet fuel has a luminosity number rating greater than 45. It is anticipated that in the near future fuels with a luminosity number less than about 52 will be unacceptable to commercial users.

The normal commercial kerosene fraction has a luminosity number that is relatively low and, therefore, must in some manner be improved prior to use as a jet fuel. Since these deficiencies of the kerosene fraction can be attributed to the presence of comparatively large quantities of high boiling aromatics, a substantial portion of these aromatics should conceivably be eliminated or converted to compounds having a lower C/H ratio if the kerosene fraction is to have an acceptable luminosity number.

In view of the knowledge of the art that the tendency of a fuel to form carbon when burned in a gas turbine engine is increased by the presence of aromatic compounds in the fuel and that the aromatic content of a fuel can be decreased by hydrogenation, it is natural to resort to hydrogenation in an attempt to improve the properties of the fuel. The hydrogenation of aromatic compounds requires the use of rather severe hydrogenation conditions, in comparison with certain other hydro-

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genation processes such as desulfurization and the conversion of olefins to saturated compounds, although not as severe as hydrocracking. Hence, it is found that the hydrogenation of a kerosene type fuel having a luminosity number of about 49 using a cobalt molybdate supported on alumina catalyst at 650° F., 500 p.s.i.g., 0.25 WHSV (weight hourly space velocity, meaning weight units of oil per weight unit of catalyst per hour) and hydrogen feed rate of 5000 s.c.f./b. (standard cubic feet of hydrogen measured at 60° F. and one atmosphere absolute pressure per barrel of oil) yields an acceptable product having a luminosity number of about 60.

In hydrogenation operations, it is important from the standpoint of economy to reduce the severity of the hydrogenation conditions as much as possible consistent with the production of a product of the required properties. In hydrogenating a kerosene type fuel under less severe conditions of temperature, pressure and space velocity it is found, as would be expected, that product quality suffers. However, in accordance with my invention, I have discovered that the hydrogen feed rate can be considerably reduced without adversely affecting product quality, providing the hydrogen feed rate is reduced sufficiently. Thus, using the other conditions of the preceding paragraph, a hydrogen feed rate of 2000 s.c.f./b. yields a product of the same quality as a hydrogen feed rate of 5000 s.c.f./b., whereas a hydrogen feed rate of 3500 s.c.f./b. does not, the product produced with the 3500 s.c.f./b. feed rate being definitely poorer.

I have also found that the hydrogenation of a kerosene type fuel having a luminosity number of about 42 using a cobalt molybdate supported on alumina catalyst at 650° F., 500 p.s.i.g., 0.25 WHSV and a hydrogen rate of 2100 s.c.f./b. shows a minor improvement of only 2 luminosity numbers, being improved from 42 to about 44. When the pressure is increased to 700 p.s.i.g. and hydrogen rate is increased to 7000 s.c.f./b., other conditions remaining constant, a product with a significant improvement in luminosity number is obtained, although the luminosity of about 48 obtained is not acceptable by anticipated standards. Further reduction in hydrogen rate to 5000 s.c.f./b., pressure 700 p.s.i.g., 650° F temperature and 0.25 WHSV, produces a product of even lower luminosity number. All of these results are as expected. A further reduction in hydrogen rate to 3500 s.c.f./b., other conditions remaining the same as in the previously mentioned run, yields a product of quality superior to that produced at either 5000 or 7000 s.c.f./b. hydrogen rate, giving a luminosity number of about 53, which is acceptable by the anticipated standards.

Since these two feedstocks were from widely different crude sources, it is not surprising to those familiar with the art that somewhat different processing conditions would be required to successfully effect a significant change in the aromatic content, and hence the burning quality. However, in both instances I found that a relatively low hydrogen rate gave unique results.

It is well known to the art that if the same degree of vaporization of the feedstock is to be maintained when the pressure is increased, either the temperature or the hydrogen rate, or both, must also be increased. Since lower temperatures favor the hydrogenation reaction, I have found it undesirable to increase the temperature beyond about 670° F. and in certain instances beyond about

650° F. Hence, to maintain about the same degree of vaporization at 700 p.s.i.g. that was obtained at 500 p.s.i.g. it is desirable to rely upon an increase in hydrogen rate only.

According to my invention hydrogenation of kerosene type gas turbine fuels with consequent improvement in burning qualities can be accomplished by contacting such fuels with a cobalt-molybdate supported on alumina catalyst at a temperature of about 620 to 670° F., a pressure of about 450 to 750 p.s.i.g., a weight hourly space velocity of about 0.1 to 1.0, and in the presence of free hydrogen supplied at a feed rate of about 1500 to 4000 s.c.f./b. of fuel charge. Generally speaking, the lower the luminosity number of the feed, the higher the hydrogen feed rate which should be used. In any event, operating conditions should be chosen within the foregoing limits to give an increase in luminosity number of at least 8. The

Table I—Continued

Luminosity number ¹ -----	49.3
Freeze point, ° F-----	-56
Flash (TCC), ° F-----	130
Sulfur, wt. percent-----	0.364
ASTM distillation:	
IBP, ° F-----	338
10-----	369
30-----	389
50-----	412
70-----	438
90-----	477
95-----	498
EP-----	516

¹ Obtained on a CRC luminometer and sometimes referred to as luminometer number. CRC designates the Coordinating Research Council of the American Petroleum Institute.

Table II

Run Numbers-----	1	2	3	4	5	6	7	8	9	10
Processing Conditions:										
Pressure, p.s.i.g.-----	500	500	500	500	500	500	250	750	500	500
WHSV-----	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.51	1.0
Temperature, ° F-----	650	650	650	650	700	750	650	650	650	650
Hydrogen Rate, s.c.f./b.-----	5,000	3,500	2,000	3,500	3,500	3,500	3,500	3,500	3,500	3,500
Inspection Tests:										
Refractive Index, n_D^{20} -----	1.4433	1.4445	1.4431	1.4450	1.4457	1.4474	1.4472	1.4385	1.4450	1.4451
Aromatics (FIA), Vol. Percent-----	10.2	12.7	10.6	12.1	16.1	21.1	15.8	4.6	12.1	12.9
Hydrogen (Beta-ray), Wt. Percent-----	14.23	14.15	14.19	14.12	14.03	13.84	13.98	14.47	14.11	14.08
Smoke Point, mm-----	28.1	26.0	27.8	26.4	23.6	20.2	24.1	33.7	26.6	26.5
Luminosity Number ² -----	61.5	58.8	60.1	55.0	54.7	43.5	51.4	72.7	58.1	58.4
ASTM Distillation-----										
IBP, ° F-----	340	335	330	339	324	301	342	320	338	337
10-----	367	362	353	364	356	337	366	352	368	366
50-----	409	405	408	410	402	392	411	402	412	409
90-----	474	468	471	477	464	459	477	466	477	474
EP-----	517	510	517	520	510	521	521	505	518	518

¹ Once through basis.

² Obtained on a CRC luminometer.

kerosene type gas turbine fuel which I hydrogenate in accordance with my invention is generally a straight run petroleum distillate fraction having an initial boiling point within the range from 275° F. to 400° F. and an end point within the range from 450° F. to 600° F. The catalyst utilized in the practice of my invention can be produced by any of the various methods for manufacturing such catalysts described in the art, such as in Byrns Patent 2,325,033. The catalyst generally consists essentially of from 2 to 5 percent by weight of cobalt oxide and from 5 to 15 percent by weight of molybdenic oxide, the balance being alumina. A suitable catalyst can also be prepared as described in Teter et al. Patent 2,898,308.

The following examples are presented to better illustrate the effects of the several process variables upon the quality of the product produced. These examples will further serve as a demonstration of the unexpected results obtained when employing a hydrogen feed rate within the range that I have discovered.

EXAMPLE I

A straight run kerosene fraction having the characteristics shown in Table I was subjected to hydrogenation under various process conditions in the presence of a cobalt-molybdate supported on alumina catalyst. The catalyst analyzed approximately 3 percent cobalt oxide and 10 percent molybdenic oxide by weight, the remainder being alumina. The operating conditions and results of various test runs are shown in Table II.

Table I
FEEDSTOCK INSPECTIONS

Gravity, ° API-----	43.2
Refractive index, n_D^{20} -----	1.4485
Aromatics (FIA), vol. percent-----	15.0
Hydrogen (beta-ray), wt. percent-----	13.91
Smoke point, mm-----	23.3

A comparison of data obtained from a series of test runs employing different hydrogen feed rates and set forth in Table II, runs 1, 2, and 3, demonstrates the effects of reducing the hydrogen feed rate. Run 1 shows the results of hydrogenating under conditions known to the art, namely 500 p.s.i.g., 0.25 WHSV, 650° F., and a hydrogen rate of 5000 s.c.f./b. As expected, the luminosity number was raised from a somewhat unacceptable 49.3 to a definitely satisfactory 61.5. As also would be expected, a decrease in the hydrogen feed rate results in a decreased luminosity number of the product as shown in run 2 utilizing a hydrogen feed rate of 3500 s.c.f./b. Unexpectedly, however, a further decrease in the hydrogen feed rate does not result in a further decrease of the luminosity number. On the contrary, as shown in the data obtained from run 3, a further decrease in the hydrogen feed rate to 2000 s.c.f./b. yields a product that is in every way comparable to that obtained employing a hydrogen feed rate of 5000 s.c.f./b. (run 1).

Runs 4 through 10 are included in Table II to illustrate the effects of varying the other process variables. Thus, runs 4, 5 and 6 illustrate the effects of temperature variation; runs 7 and 8 pressure variation; and runs 9 and 10 space velocity variation. These data show that decreasing reaction severity results in a lower luminosity number.

EXAMPLE II

A straight run kerosene fraction having the characteristics shown in the column entitled "Feed" of Table III was subjected to hydrogenation under various process conditions in the presence of the cobalt-molybdate supported on alumina catalyst of Example I. The operating conditions and results of the various test runs are shown in Table III.

Table III

Run Numbers.....	Feed	1	2	3	4	5	6	7
Processing Conditions:								
Pressure, p.s.i.g.....		500	500	700	700	700	700	700
WHSV.....		0.25	1.0	0.25	0.25	1.0	0.25	0.25
Temperature, ° F.....		650	650	650	700	650	650	650
Hydrogen Rate, s.c.f./b.....		2,100	2,100	3,500	3,500	3,500	5,000	7,000
Product Inspections:								
Refractive Index, n_D^{20}	1.4577	1.4535	1.4547	1.4502	1.4520	1.4532	1.4510	1.4500
Aromatics (FIA), Vol. Percent.....	18.8	15.6	17.3	11.4	15.5	15.3	12.1	11.6
Hydrogen (Beta-ray), Wt. Percent.....	13.36	13.63	13.49	13.79	13.65	13.62	13.66	13.78
Smoke Point, mm.....	18.8	20.0	18.1	23.3	21.3	17.9	22.2	22.2
Luminosity Number ¹	41.7	43.8	40.2	52.9	46.1	42.2	45.6	47.7
ASTM Distillation—								
IBP.....	308	333	336	336	326	308	336	346
10.....	376	370	374	368	367	370	366	372
50.....	418	414	415	412	413	410	412	410
90.....	465	460	460	460	460	456	457	456
EP.....	498	498	499	498	499	492	494	492

¹ Obtained in a CRC luminometer.

A comparison of data obtained from two test runs (runs 1 and 2) employing approximately the same processing conditions used in Example I shows little improvement in the luminosity number. As would be expected, raising the pressure to 700 p.s.i.g. and 7000 s.c.f./b. hydrogen feed rate (run 7) resulted in a significant improvement in luminosity number, although the improvement is not considered satisfactory. As also expected, a decrease in the hydrogen feed rate to 5000 s.c.f./b. resulted in a decreased luminosity number of the product as shown in run 6. Unexpectedly, however, a further decrease in the hydrogen feed rate does not result in a further decrease in the luminosity number. On the contrary, as shown in the data obtained from run 3, a further decrease in the hydrogen feed rate to 3500 s.c.f./b. yields a product with an acceptable luminosity number of about 53 and is superior to that obtained employing a hydrogen feed rate of 7000 s.c.f./b. (run 7).

Runs 2, 4 and 5 are included to illustrate the effects of varying the other process variables. Thus runs 2 and 5 illustrate the effect of space velocity at two different pressure levels, as well as effect of pressure at another space velocity level. Run 4 illustrates the effect of temperature. These data show that decreasing reaction severity results in a lower luminosity number.

I claim:

1. A process for the production of a fuel of improved burning qualities when burned in a gas turbine engine which comprises contacting a straight run kerosene type petroleum distillate fraction with a cobalt-molybdate supported on alumina catalyst at a temperature within the range from about 620° F. to 670° F., a pressure within the range from about 450 p.s.i.g. to 750 p.s.i.g. and at a weight hourly space velocity within the range from about 0.1 to 1.0 while in admixture with hydrogen fed in amount within the range from 1500 to 4000 standard cubic feet per barrel of said distillate fraction whereby the luminosity number of said fraction is increased at least 8.

2. The process of claim 1 in which the distillate fraction has an initial boiling point within the range from 275° F. to 400° F. and an end point within the range from 450° F. to 600° F.

References Cited in the file of this patent

UNITED STATES PATENTS

2,810,004	Morbeck et al.	Oct. 15, 1957
2,899,383	Hill	Aug. 11, 1959
2,904,500	Beuther et al.	Sept. 15, 1959