Refining of Turbine Fuels by Modern Hydrotreating

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This paper reviews the present status of technology for removing sulfur compounds and hydrogenating aromatics in jet fuels, often designated as turbine fuels. The newer technique of catalytic hydrotreating will be emphasized because of its effectiveness in removing sulfur as well as nitrogen compounds, its flexibility in refinery applications, and its ability to upgrade other fuel characteristics, such as smoke point, aromatics content and thermal stability.

Background on Turbine Fuel

ACCORDING to one forecast, turbine fuel consumption for civil aviation is expected to increase from half a million barrels per day in 1968 to a million barrels per day by 1975, or about 15% per year. Past and projected jet fuel consumption is shown in Fig. 1 and the insert lists some milestones in commercial jet aircraft development. Another forecast calls for a growth rate of only 8% per year during the period 1972–1975.

The evolution in turbine or jet fuel specifications is observed in Table 1. Starting with JP-3 back in 1947, we find requirements that relate to engine performance, aircraft design and combustion-related corrosion. Operational problems were encountered with JP-3 in connection with fuel loss during fast climb and fuel flow at high altitude (low temperature). Hence the development of JP-4, which is the major fuel used by the Air Force. Moreover, the safety aspect of ship-board (Navy) handling led to the devlopment of JP-5. The importance of thermal stability was recognized with the advent of JP-6 and the commercial fuels: Type A, Type A-1, and Type B. Thermal stability is a measure of the fuel's ability to absorb heat at elevated temperature without depositing coke on heat exchangers or burner nozzles. This property is especially important in high performance aircraft where the fuel serves as a cooling agent prior to combustion. This function may become increasingly important because of the aerodynamic heating encountered during supersonic flight. Figure 2 shows the relation of temperature to Mach number. For a flight speed up to Mach 3, JP-6 fuel with its higher thermal stability appears suitable.

With this background, the typical turbine fuel specs shown in Table 2 become more meaningful.

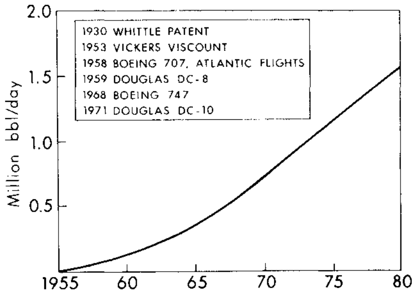

Fig. 1 U.S. demand for commercial turbine fuel for period 1955–1980.

Table 1 Evolution of jet fuel specifications

Military		
1947	JP-3	Smoke point introduced. Sulfur about 0.4%.
1951	JP-4	Lower volatility to avoid fuel loss during fast climb. Freezing point = −76°F max. Mercaptan sulfur reduced from 0.005 to 0.001 wt%.
1957	JP-5	Higher flash point (140°F) for Navy use.
1961	JP-6	Thermal stability introduced for higher altitude and higher speed aircraft.
1970	JP-7	Increased luminometer number and thermal stability for advanced military aircraft.
Commercial		
1959	Type A	Kerosene type like JP-5. Luminometer number introduced. Freezing point = −40°F max.
1959	Type A-1	Freezing point lowered to −58°F for transoceanic flights. Sulfur equal or less than 0.3%.
1959	Type B	Wide cut JP-4 to expedite supply.

Refining by Modern Techniques

Early refining of kerosine and jet fuel largely involved wet chemical processing. This included acid and caustic washing, solvent extraction and percolation through porous beds.

Catalytic hydrotreating has largely replaced wet chemical processing because of its ability to effectively remove sulfur and other contaminants and still achieve high product yields without generating a waste disposal problem. Hydrotreating is a catalytic phenomenon. The catalyst to be used must selectively "speed up" the reaction of hydrogen with certain compounds containing sulfur and nitrogen but not those compounds containing carbon and

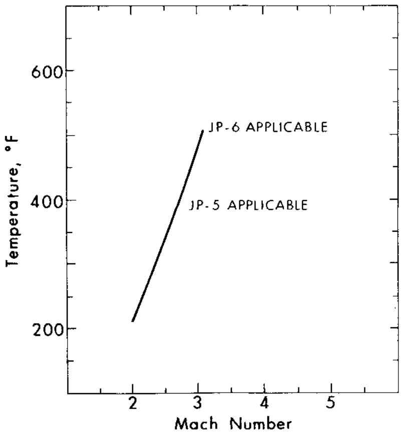

Fig. 2 Effect of aerodynamic heating.

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Table 2 Partial list of ASTM specifications for aviation turbine fuels

	Minimum	Maximum
Gravity, °API	39.0	51.0
Heat of combustion, BTU/lb	18400	...
ASTM distillation, °F		
10%	...	400
50%	...	450
EP	...	550
Flash point, °F	105	150
Freeze point, °F		
Jet A	...	−36
Jet A-1	...	−54
Alternate combustion properties		
1) Luminometer number	45	...
2) Smoke point, mm	25	...
3) Smoke point, mm	20	...
Naphthalenes, vol%	...	3
Aromatics, vol%	...	20
Sulfur, total, wt%	...	0.3
Thermal stability @ 300–400°F		
Filter ΔP, in Hg	...	12
Deposit code	...	3

Table 3 Typical cobalt molybdate hydrotreating catalyst

Composition, wt%	
CoO	6
MoO_3	15
SiO_2	4
Al_2O_3	75
Surface area, m^2/g	250
Bulk density, lb/cf	45
Form	Extrudate
Extrudate size, in.	$^1/_{16} \times {}^3/_{16}$

Table 4 Upgrading of turbine fuel by severe catalytic hydrotreating

Property	Untreated turbine fuel	Hydrotreated turbine fuel
Gravity, °API	39.4	43.0
Distillation, °F		
10%	374	358
50%	416	420
End point	495	505
Smoke point, mm	18.0	28.0
Luminometer number	44	64
Total sulfur, wt%	0.19	<0.001
Erdco thermal stability,		
ΔP, in. Hg/5 hr	>12	Nil
Freeze point, °F	−65	−65
Net Btu/lb	18,500	18,700
Aromatics, vol% by F.I.A.	18.4	0.5

hydrogen only. This is illustrated in Fig. 3 where the proper catalyst will accelerate reaction 1 instead of reaction 2. In other words, a selective hydrotreating catalyst is desired instead of a hydrocracking catalyst.

For those cases where the turbine fuel comes from a crude oil of high aromatics content, additional catalytic treating may be required. This involves a second catalyst which is selective toward the hydrogenation of aromatics, as shown by reaction 3.

Development of an active desulfurization catalyst evolved from a combination of cobalt and molybdenum oxides dispersed on a high surface area carrier of silica-aluminum oxide. An example of this kind of catalyst, taken from the patent literature, is shown in Table 3. The enormous surface area afforded by the fine pores of the catalyst can be appreciated when we realize that 1 gram contains approximately 300 square yards of surface. This catalyst resembles one of the highly active long-lived, low-cost catalysts used in the "Unionfining" process which is licensed by the Union Oil Company of California.

Figure 4 is a simplified flow diagram showing how the described catalyst is used on a refinery scale. Feedstock or unrefined jet fuel and hydrogen are preheated by exchange with reactor effluent and then heated to the desired reaction temperature by a fired heater. In the reactor, the sulfur is chemically removed from the sulfur compounds and made into hydrogen sulfide (H_2S). As a volatile gas, this hydrogen sulfide is easily removed by stripping in the product stripper. The reactor product is heat exchanged with reactor feed, cooled and sent to a high pressure separator. Hydrocarbon phase from the separator goes to a stripper column where hydrogen sulfide and light hydrocarbons (C_1–C_4) are removed.

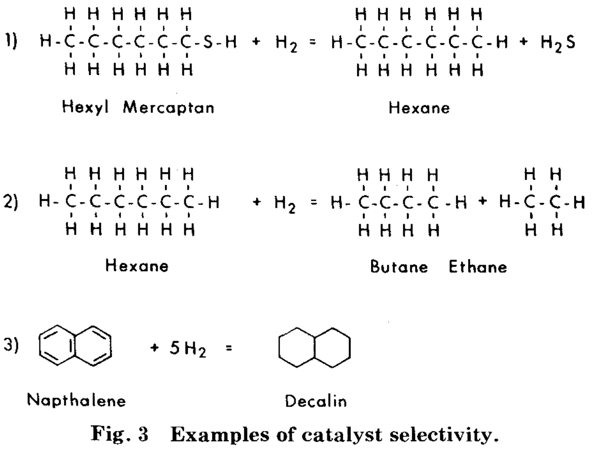

Fig. 3 Examples of catalyst selectivity.

If the unrefined jet fuel had contained nitrogen compounds as well as sulfur compounds, then ammonia (NH_3) as well as hydrogen sulfide produced in the reactor would be removed by the stripper.

Examples of Upgrading Turbine Fuels

A. Sulfur Removal and Partial Aromatics Saturation

A specific example of catalytic hydrotreating to upgrade a turbine fuel is shown in Table 4. We observe the following major changes which relate to a superior fuel.

1) Increase in smoke point and luminometer number. This means clean, efficient combustion.

2) Practically complete removal of sulfur. This eliminates both engine corrosion and air pollution caused by sulfur oxides. Also, a sulfur-free fuel tends to be an odorless fuel.

3) Improvement in thermal stability. This means a reduction in engine fuel system deposits and coke.

All this is achieved without an adverse effect on freezing point or heat of combustion.

The reduction in aromatics content by catalytic hydrogenation has been cited. Also, Table 4 suggests that im-

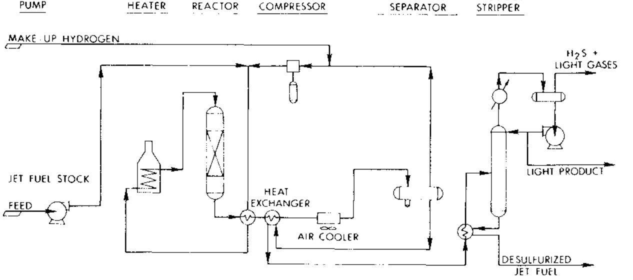

Fig. 4 Unionfining process simplified flow diagram.

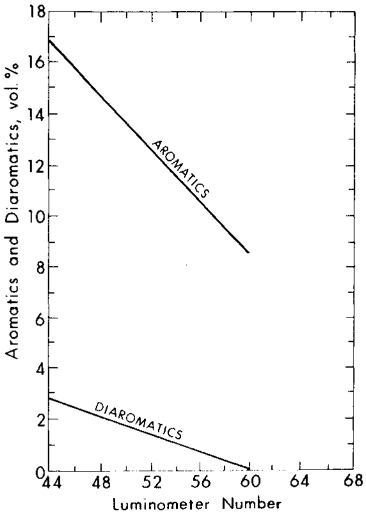

Fig. 5 Effect of aromatics and diaromatics on luminometer number.

provement in smoke point and luminometer number result from a decrease in aromatics content. This relation is indicated in Fig. 5, where the deleterious effect of mono- and diaromatics (for example, naphthalene) is very pronounced. Not shown on the slide is the improvement in color and color stability achieved by hydrotreating. These properties relate to customer acceptance and involve the removal of nitrogen compounds.

Selection of processing conditions is generally based on the nature of the feedstock, activity of the catalyst, the degree of conversion desired, and on economic considerations. However, the process conditions generally are in the ranges given in Table 5. Pressures are 300–800 psig, space velocities are 0.5–4.0 hr^{-1}, hydrogen recycle rates are 300–3000 scf/barrel of hydrocarbon feed and reactor temperatures are 575–775°F.

Space velocity *(SV)* is a measure of catalyst nominal contact time *(t)* if the feedstock were all in liquid phase, and is obtained by dividing the hourly feed volume by the catalyst volume. Accordingly, when $SV = 2.0$ hr^{-1}, $t = 0.50$ hr or when $SV = 4.0$ hr^{-1}, $t = 0.25$ hr.

A quick impression of the influence of reactor variables on the aromatic content of the jet fuel product is obtained from Fig. 6. One observes that the desirably low aromatic contents are obtained by 1) increasing the pressure, 2) lowering the space velocity, and 3) approaching an optimum temperature in the vicinity of 700°F.

B. Deep Aromatic Saturation

For feedstocks high in aromatics, such as those obtained by hydrocracking of cycle oils from catalytic crackers, the cobalt-molybdate catalyst mentioned in the previous section requires very high pressures for aromatics hydrogenation. This approach is usually uneconomical.

A different type of catalyst involving a noble metal, like platinum-on-alumina, has the ability to hydrogenate aromatics at much lower pressures and at lower temperatures which are thermodynamically more favorable. The Union Oil Company of California has developed such a catalyst known as "Unisar" catalyst, which is particularly active because of its high metal dispersion on a special support. The use of catalyst in the "Unisar" process can give the high reduction of aromatics shown for a hydrocracker jet stock in Table 6, while operating at 400–600°F and 400–1000 psig. Note the "swelling factor" that leads to 104 barrels of product from 100 barrels of feed. Also, the catalyst does not produce "light ends" or lower the 10% boiling point. In order to avoid payment of gasoline taxes in some states, the 10% point of turbine fuel must have a minimum of 347°F.

Table 5 Typical unionfining conditions

Pressure, psig	300–800
Temperature, °F	575–775
Space velocity, hr^{-1}	0.5–4.0
Recycle gas, scf/barrel	300–3000

Table 6 Unisar processing of hydrocracker jet stock

	Feed	Product
Gravity, °API	37.5	41.0
ASTM D-86 distillation, °F		
10%	351	349
50%	411	406
Maximum	528	530
Sulfur, ppm	10	Nil
Aromatics, wt%	42	14
Smoke point, ASTM, mm	15	23
Luminometer number	30	48
Freezing point, °F	−50	−51
Yields		
Turbine fuel yields, vol% feed		103.9
Chemical hydrogen consumption, scf/bbl feed		680

Economics of Hydrotreating

From the standpoint of both capital investment and operating charges, hydrotreating is a relatively low cost catalytic process. Detailed economics will reflect the nature of the feedstock, reactor conditions, and product objectives.

Over a wide range of Unionfining applications, plant costs for a 10,000–20,000 barrel per stream day unit have varied from $100–$200 per barrel of daily throughput. Operating costs are typically 5–13¢ per barrel, of which catalyst costs are only 0.2–0.9¢ per barrel.

More specifically, the cost in refining a 0.4% sulfur jet fuel to a 0.1% sulfur product would be 12.3¢ per barrel. The incremental cost to obtain a 0.05% sulfur product would be 0.8¢ per barrel. To obtain a 10 ppm sulfur product would cost another 1.2c per barrel.

Summary

The background for turbine fuel specifications has been presented on a functional basis and related to the ability of hydrotreating catalysts to remove sulfur, aromatic and diaromatic compounds by means of chemical combi-

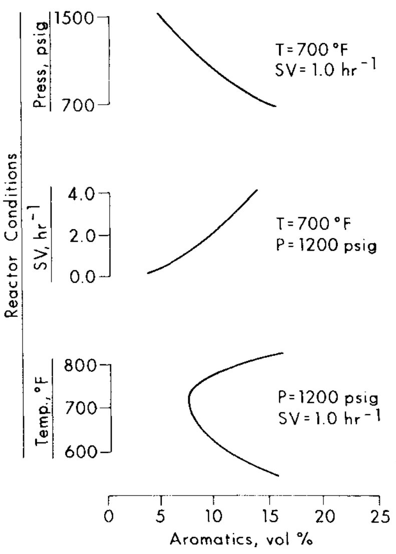

Fig. 6 Effect of process variables on aromatics content.

nation with hydrogen. This has been specifically considered with major fuel properties such as sulfur content, smoke point and thermal stability.

The extensive degree of sulfur removal by a cobalt molybdate catalyst and aromatics saturation by a noble metal catalyst have been cited. This plus the effect of temperature, pressure and other reactor variables have illustrated the flexibility of the process, which gives uniquely high yields of quality product without a waste disposal problem.

Engineering Notes

ENGINEERING NOTES are short manuscripts describing new developments or important results of a preliminary nature. These Notes cannot exceed 6 manuscript pages and 3 figures; a page of text may be substituted for a figure and vice versa. After informal review by the editors, they may be published within a few months of the date of receipt. Style requirements are the same as for regular contributions (see inside back cover).

Flutter Test Analysis in the Time Domain Using a Recursive System Representation

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Introduction

FLUTTER test analyses usually involved determining estimates of modal frequency and damping for the system under consideration and then following trends of these results with speed and Mach number to check for a possible flutter condition. Developments in this field are aimed at reducing test and analysis time and improving the accuracy of results in the presence of noise (i.e., turbulence).

Recently there have been interesting developments toward rapid analysis with two methods, the "Least Squares Identification" method[1,2] and the "Correlation Fit" method, described for the first time in this Note. They extract the results directly and automatically from the time histories without resort to the frequency domain and the analysis of vector plots. Both these methods involve choosing a model for the unknown system, representing it recursively,[3] and matching it to the data by curve fitting. It is believed that their noise rejection should be at least as good as that for other methods such as the Autocorrelation and Crosscorrelation methods.[4]

The Least Squares Identification method fits the assumed model directly to the time histories by the method of least squares.[5] In this Note, the method is examined and shown to be equivalent to an exact fit to the first few lag values of the autocorrelation of response and the crosscorrelation of excitation and response. The need for decimation, mentioned in Ref. 1, is explained.

The Correlation Fit method also is described. This is believed to be new and is still at an early stage in development. A "model match" is carried out by writing the autocorrelation and cross correlation functions in terms of the unknown model coefficients and carrying out a simultaneous least squares fit to a chosen number of lag values of these correlation functions from which the coefficients are determined. Thus the Least Squares Identification method is shown to be a special case of the Correlation Fit method.

Basic Test and Analysis Procedure

The system of interest (such as an aircraft) is excited with any known input, though the methods can be adapted easily to cope with an unknown input. A sinusoidal frequency sweep is a suitable input since it tends to separate the modes. The response is measured and the signals sampled. Normally, the procedure is to choose segments of these data, each containing only one or two dominant modal response peaks.

A model transfer function is assumed for the system within each segment and a hold[3] is included. Using Z transform theory,[1-3] a recursive relationship between sampled response and excitation (y_j and x_j, $j = 1,2 \ldots L$) can be written in the form

$$y_j = \sum_{i=1}^{N} a_i y_{j-i} + \sum_{i=0}^{M} b_i x_{j-i} \tag{1}$$

where a_i and b_i are the coefficients defining the denominator and numerator of the model Z transfer function and hence the modal frequencies and dampings.

With no noise and a correctly chosen model, Eq. (1) is satisfied exactly by the measured values and therefore can be solved for the coefficients. However, where noise is present or the model does not correspond to the real system, the equation can be thought of either as giving an estimated response $\hat{y}_j$ different from the measured value y_j or as an approximate relationship between measured values. Thus an estimate of the coefficients can be obtained from this equation through a curve fit or model match, carried out in different ways by the two methods.

Least Squares Identification Method

If a segment that starts at point NS and finishes at NF is selected from the L point measured excitation and response records, and the general Nth order model in Eq. (1) is chosen, then the procedure[1] is to write this equation for each point in matrix form as

$$\begin{Bmatrix} y_{NS} \\ y_{NS+1} \\ \vdots \\ y_{NF} \end{Bmatrix} = \left\{ \begin{matrix} y_{NS-1} & \cdots & y_{NS-N} \\ y_{NS} & \cdots & y_{NS-N+1} \\ \vdots & & \vdots \\ y_{NF-1} & \cdots & y_{NF-N} \end{matrix} \right. \times \left. \begin{matrix} x_{NS} & \cdots & x_{NS-M} \\ x_{NS+1} & \cdots & x_{NS-M+1} \\ \vdots & & \vdots \\ x_{NF} & \cdots & x_{NF-M} \end{matrix} \right\} \begin{Bmatrix} a_1 \\ \vdots \\ a_N \\ b_0 \\ \vdots \\ b_M \end{Bmatrix} \tag{2}$$

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