

# STUDYING ON THE JET FUEL TREATING PLANT FOR MAXIMUM EFFICIENCY

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## Abstract

Environmental and international specification standard of Jet fuels must meet very stringent, because they are used by airlines from all over the world that fly to the country where jet fuel is produced.

There are many important aspects of chemical treating naphtha and kerosene fractions with sodium hydroxide solutions (caustic) for the removal of naturally occurring contaminants in the production of jet fuels.

This article is presented, the method of aviation turbine fuel treatment and then it is investigated the effectiveness parameter to obtain suitable operating condition.

**Keywords:** treatment, refinery, jet fuel, upgrading

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## 1. Theoretical background

The chemical treating is used in refinery plant for naphtha and kerosene fractions to jet fuels production. It is often necessary to meet acidity, mercaptan and other specifications required for the upgrading of these fractions to jet fuel products

One of the fastest growing refinery product market demands is jet fuel, often called turbine fuel. Air travel is projected to continue growing in popularity in the years to come and the refinery that produces jet fuel at the lowest cost will be in the best position to supply this market. A refiner that produces high quality jet fuels can find attractive markets for their product throughout the world.

Jet fuels must meet very stringent, international specifications (see table I) because they are used by airlines from all over the world that fly to the country where jet fuel is produced. As is readily apparent to those who are familiar with caustic treating, some of these specifications are not affected in any way since the compounds affecting the specifications are not caustic extractable. Aromatics, olefins, smoke point, sulfur content, and freeze point are such specifications <sup>[1-3]</sup>.

The refinery production of jet fuel varies from simply withdrawing a side-stream product from the crude oil fractionator that requires no additional treating or cleanup; to withdrawing a side-stream product that requires only minimal cleanup such as clay filtration; to withdrawing a side-stream product that requires caustic treating followed by water washing, salt drying, and clay filtration; and, finally, to withdrawing a side-stream product that must be hydrotreated before it can meet jet fuel specifications <sup>[4]</sup>.

Hydrotreating involves a much greater capital investment (10 to 20 times) and requires much higher operating costs (20 to 50 times) than "wet treating" which is the phrase often used to denote caustic treating with the attendant cleanup processes. For these reasons, refineries avoid hydrotreating whenever possible. However, hydrotreating can produce jet fuel from most crude oils, whereas wet treating is limited to jet fuels, which already meet the specifications not affected by caustic treating.

**Table (I): Typical jet fuel specifications property**

Specification	Valve	Test Method
Appearance	Clear, bright and visually free from solid matter and insoluble water at ambient temperature	Visual
Total Acidity, max. mg KOH/g	Commercial, Jet-A: 0.1 Military: 0.015	ASTM D 3242-93
Mercaptan Sulfur, max. wt. %	Commercial, Jet-A: 0.003 Military: 0.001	ASTM D 3227-99
Total Sulfur, max. wt. %	0.30	ASTM D 4294-98
Aromatics, max. vol. %	20	ASTM D 1319-98
Flash Point, min. °C	38	ASTM D 56-98a
Density @ 15°C, kg/m <sup>3</sup>	778 - 840	ASTM D 1298-99 ASTM D 4052-96
Freezing Point, max °C	- 40	ASTM D 2386-97
Viscosity @ -20°C, max. mm <sup>2</sup> /s	8.0	ASTM D 445-97
Net Heat of Combustion, min. MJ/kg	42.8	ASTM D 2624 – 98
Smoke Point, min. mm	20	ASTM D 1322-97
Corrosion, Copper Strip, 2 hr @ 100°C max.	No.1	ASTM D 130-94
Existent Gum, max. mg/100 mL	7	ASTM D 381- 99
Specific Electrical Conductivity, pS/m	50-450	ASTM D 2624 98
Water Separation Characteristics	1b	ASTM D 1094 -99
Water reaction interface, max, bale		

## 2. Principles of caustic treating

The removal of any impurity involves mass transfer or, in the case of caustic treatment, the movement of the impurity from the hydrocarbon to the aqueous solution. The rate at which this mass transfer occurs is the product of three independent variables:

$$M = KxAxC \quad (1)$$

Where K is the mass transfer coefficient for the given hydrocarbon and aqueous system, A is the amount of surface area available for the impurity to pass from the hydrocarbon to the aqueous phase, and C is the concentration driving force impelling the impurity to leave the hydrocarbon and enter the aqueous phase.

In the conventional treating mechanism, devices such as mix valves and static mixers create interfacial surface by depressive mixing to generate droplets of one phase in the second phase. The outside surface of each droplet provides the mass transfer surface. However, the sphere is the shape with the least surface area per unit volume of any other shape the very opposite condition demanded for high mass transfer rates.

To create the most interfacial surface area possible from a given volume, considerable sheer energy must be imparted to form as many small droplets as possible.

In the case of caustic treating systems, small droplets of caustic solution in the hydrocarbon increase the rate of mass transfer. Small droplets, however, have the disadvantage of taking longer to separate or settle out of the hydrocarbon, increasing the difficulty of the next essential operation in any treating job, which is to separate the aqueous phase from the treated hydrocarbon.

The most frequently encountered problem with treating systems in the oil industry is caustic carryover with the treated hydrocarbon. Settlers associated with depressive mixing must be quite large to avoid aqueous phase carryover. Stokes Law can be used to size the settler once the caustic droplet size is known. Quite often, settlers are undersized for economic reasons.

As hydrocarbon market demand grows, and throughputs must be increased through the settler, the settling time becomes even more inadequate and many more unsettled caustic droplets remain in the treated hydrocarbon. The presence of caustic in the treated hydrocarbon can cause multiple problems

and, if allowed to go unchecked, can result in a loss of product acceptability in the market.

The first step usually taken when caustic carryover becomes unacceptable is to input less mixing energy, thus creating larger droplets, which settle more rapidly. This diminishes mass transfer surface area (A), which reduces the mass transfer rate and treating efficiency. Quite often, decreasing the caustic concentration of the treating solution will reduce caustic carryover. This diminishes the equilibrium constant (K), which, in turn, reduces the mass transfer rate and treating efficiency. At some point, as treating efficiency diminishes, the treating operation cannot afford further reductions in mixing energy or caustic concentration.

To reduce caustic carryover must be used more efficient method of creating interfacial surface area that would avoid dispersion while at the same time allowing equilibrium constants and concentration driving force (C) to be increased<sup>[5-6]</sup>.

### 3. Process description

The refinery production of jet fuel has several steps: caustic treating followed by water washing, salt drying, and clay filtration; and, finally, to withdrawing a side-stream product that must be hydrotreated before it can meet jet fuel specifications. Because high capital investment and also higher operating cost of hydrotreating process, the refineries avoid this process whenever possible and caustic treating is preferred. However, hydrotreating can produce jet fuel from most crude oils, whereas caustic treating is limited to jet fuels, which already meet the specifications not affected by caustic treating. Figure 1 shows process flow diagram of jet fuel treating unit. There are two main steps in this process, total acidity reduction, and mercaptan oxidation.

The processing step required when total acidity must be reduced is a weak caustic pre-wash, which is designed specifically to extract strongly acidic compounds such as H<sub>2</sub>S, but in particular naphthenic acids, from the jet fuel.

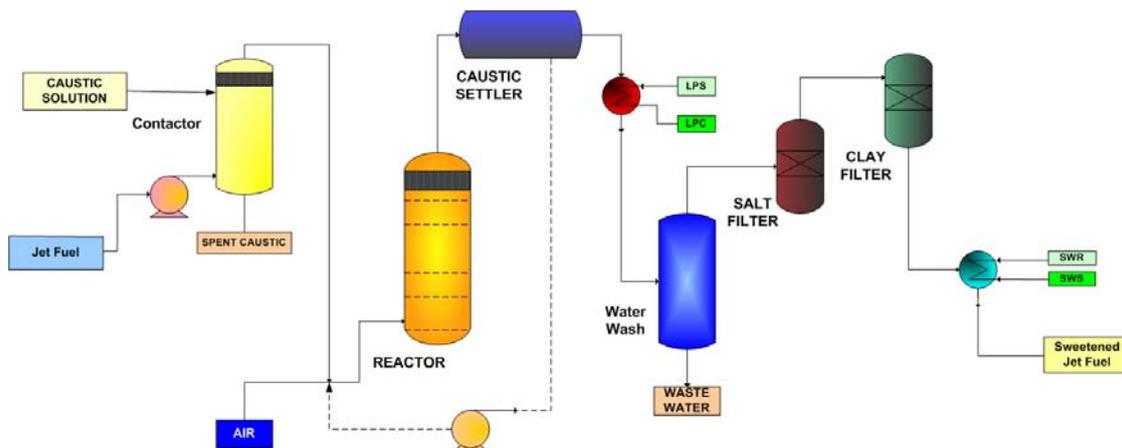
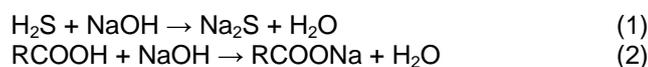


Fig (1): process flow diagram of jet fuel treating unit.

The typical neutralization number specifications vary from 0.005 Mg KOH/g of hydrocarbon to as high as 0.10 depending on the product market or downstream process requirements. In addition, the removal of H<sub>2</sub>S and light mercaptans (if any) assures that the product jet fuel will meet the copper and silver strip corrosion specifications.

By reducing the total acidity of the jet fuel, the pre-wash also provides a more easily sweetened feedstock for the mercaptan oxidation process that follows. The Contactor allows the caustic with hydrogen sulfide and naphthenic acids to react without dispersion of phases. This reactions form sulfide sodium and sodium naphthenate, respectively, the chemistry of which are shown below:



The Contactor is a static contacting device that produces non-depressive contacting of the caustic and hydrocarbon phases and improves the removal of acidic impurities from the hydrocarbon stream. This prevents emulsion formation and results in minimum caustic carryover and high efficacy of the caustic solution.

The contactor, containing a multitude of fibres, provides a large amount of interfacial surface area, which increases the mass transfer rate. At the same time, the aqueous phase is constrained to the fibre material by surface tension forming a film on each fibre that contacts, but never mixes with, the hydrocarbon phase. Consequently, separation of phases becomes a simple and efficient step in the process.

The typical jet fuel specifications or targets for neutralization number reduction are shown in table II.

Table (II): Acidity of Treated Jet Fuels (Mg KOH/g)

Specification	Content
Commercial Jet Fuel (JP-1A)	< 0.10
Military Jet Fuels (JP-4, JP-5, NATO F-35)	< 0.015
Jet Fuel to a Solid Bed Sweetening Reactor	< 0.005

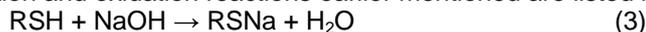
Sodium naphthenate has a great tendency to emulsify with the jet fuel producing a stable emulsion sometimes called a "rag" or soap, which is very difficult to break, and certainly not in the time provided in most conventional caustic treating systems. Therefore, entrainment of the caustic phase can be excessive when dispersive mixing devices are used. If these soaps get into downstream mercaptan sweeteners, they can adversely affect their performance. These soaps also will cause the jet fuel to fail other specifications such as water separation index if allowed to remain in the finished jet fuel product. Therefore, this step is critical to successful jet fuel production.

The typical conventional mixer settling system with electrostatic precipitation often employed by competitors provides the kind of mechanism that is conducive to creating emulsions particularly with highly naphthenic kerosene.

With proper reduction of the neutralization number, any mercaptans contained in the jet fuel can then be oxidized to disulfide oils in a separate system. If sweetening were not required then the jet fuel would pass on to additional product cleanup steps.

After this section, Naphtha is sent to extractor, where low molecular weight mercaptans C<sub>1</sub>-C<sub>2</sub> and partially mercaptans C<sub>3</sub> are extracted with 15% caustic solution.

The mercaptan extraction and oxidation reactions earlier mentioned are listed below:



Since there is no sulfur removal involved as such, the inlet and outlet total sulfur of the sweetened jet fuel stream will remain the same. The sweetening process must reduce the mercaptan sulfur content of the jet fuel to 10 wppm for military jet fuel or 30 wppm for commercial grade of jet fuel.

Naphtha is sent from the top of the extractor to caustic separator vessel. The caustic solution containing mercaptides is sent from the bottom of the extractor to the regeneration section into the caustic solution degasser vessel. Caustic regeneration is carried out in a common regenerator reactor.

High molecular weight mercaptans C<sub>3</sub><sup>+</sup> are hardly extracted with aqueous caustic solution, but are easily oxidized to disulfides over activated carbons in the presence of catalysts and 2% caustic solution following reaction:



Jet fuel treating differs from LPG and naphtha treating because of additional product quality specifications applied to it; such as color stability, haze, water interface reaction, and Water Separation Index Modified (WSIM). In order to meet these more stringent specifications, additionally processing steps are required.

The sweetening process must reduce the mercaptan sulfur content of the jet fuel to 10, 30 ppm (wt), for military jet fuel and commercial grade of jet fuel, respectively.

Normally, jet fuel blend stocks have sufficiently high concentrations of the heavier mercaptans such that the 10 to 30 wppm desired product level cannot be met with liquid sweetening system alone, thus additional sweetening capability is required.

In this condition, it is Initially applied a liquid/liquid sweetening step, then it is followed by a second stage fixed bed of activated carbon that has been impregnated with caustic and oxidation catalyst. Both steps take place in a single vertical reactor.

After air injection, the jet fuel flows through a Contactor, for removal of the lighter and easier to oxidize mercaptans. The jet fuel then passes upward through the caustic/catalyst impregnated carbon bed installed within the top section of the separator vessel where virtually complete mercaptan oxidation is accomplished to achieve the desired mercaptan sulfur level of the product.

In the case of jet fuel treating, the system can be operated with a small fresh caustic makeup stream continuously added by a metering pump and removed on level control. Rather than being wasted, this small discharge caustic stream becomes the continuous fresh caustic addition to the upstream pre-wash stage.

#### 4. Case study

Table (III) is showed the feed specification. The treating unit is simulated and then effectiveness parameters are suddied to obtain suitable condition for maximum efficiency.

Table (III): Feed specification

FEED		
Parameter	Case 1	Case 2
Feed flow rate (BPD)	15000	8000
Pressure (Bar g)	5.4	6.2
Temperature (° C)	42	36
Specific gravity, 15°C	0.78-0.8	0.78-0.8
Acid Number, mg KOH/gm	0.15	0.06
ASTM D-86 boiling range (IBP / FBP), °C	160 / 245	155/240
H <sub>2</sub> S as S, ppm (wt)	1 - 1.2	1 -1.2
Water content, ppm (wt)	100-150	100-150

Figure (2) is showed the acid number ratio (acid No. Product / acid No. Feed) versus reaction time. The feed and dilute caustic solution (1.5 to 3 wt %) is mixed to extraction of the naphthenic acids, then dispersed phases were fed into the vertical vessel to separate. The residence time is considered 10-15, considerable unsettled caustic and emulsions produced by the mixing mechanism were carried out with the kerosene into a downstream bender treater used to oxidize mercaptans, thus causing this unit to malfunction. Only about 20% of the available caustic alkalinity was being utilized.

If a Contactor was installed in the top of the vessel to replace the mix valve method of contacting and stronger caustic (4-7%) was circulated through the Contactor.

The neutralization number of the treated product was reduced to 0.005, caustic carryover and emulsion formation was eliminated, and the downstream bender treater's operations significantly improved.

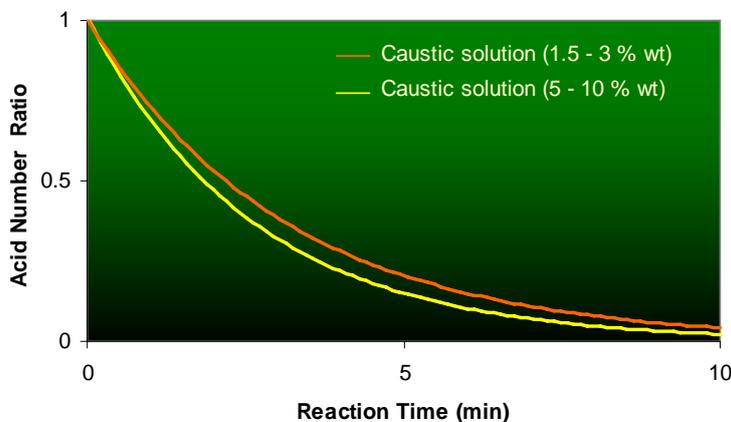


Fig (2): The curve of Acid number ratio versus Reaction Time

The lower acid content of the product from the unit also eliminated emulsions that previously formed in the bender from unreacted naphthenic acids at the previous 0.01 targets. Around 90% of the available caustic alkalinity was utilized, thus reducing NaOH consumption by 96%. The use of less caustic and higher strength caustic resulted in 97% reduction in the quantity of spent caustic produced. Figure (3) illustrates Mercaptans residue after treatment versus reaction time for the studied cases.

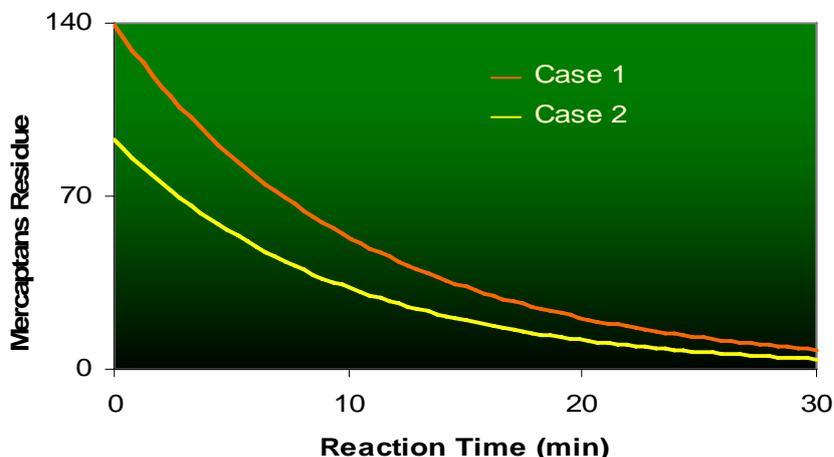


Fig (3): Mercaptans Residue curve versus Reaction time

This method can be operated in the batch or continuous mode of fresh 5-10 Bé caustic addition, but the most common mode is continuous addition by metering pump and continuous withdrawal of spent caustic on level control. Caustic recycle amounting to 5-20% of the hydrocarbon rate is always provided to assure high spending of the final caustic solution. High spending and strong caustic minimize fresh caustic use and even more importantly it reduces the amount of spent caustic volumes, which in many parts of the world is more expensive to dispose of than the cost of fresh caustic. If sweetening were not required then the jet fuel would pass on to additional product cleanup steps.

Since there is no sulfur removal involved as such, the inlet and outlet total sulfur of the sweetened jet fuel stream will remain the same.

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