

TransFinning™ – A NOVEL PROCESS FOR LOW SULFUR FUELS

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Abstract

The production of ultra low sulfur (ULS) gasoline and diesel, at a cost that is sustainable long term and in quantities that will continue to meet the demands of U. S. drivers, is potentially the single most significant and costly challenge that will be faced by the refining industry during this decade. On one hand, sulfur in fuels is a known problem. It is not only directly responsible for increased levels of NO_x in exhaust gases; but it is also a poison for many of the newer catalytic converters that are being introduced by automakers. Paradoxically, supplies of crude oils are becoming increasingly heavier and more sour, thus requiring more processing. As a result, refiners are already having to hydrotreat feeds more severely just to stay at the current sulfur levels.

Considerable effort is being expended by refiners and other organizations to develop technology that will allow them to meet the mandated sulfur specifications of 30 ppm S for gasoline and 15 ppm S for diesel on time. New lower pressure naphtha (gasoline) hydrotreating technology is being developed and capital funds are already being allocated to build additional higher pressure distillate hydrotreaters. In addition, reactive distillation, adsorption and pervaporation-based membrane technologies have all been announced. There is general agreement in the industry that the major hurdle is not the initial reduction of sulfur in gasoline to 120 ppm and diesel to 100 ppm but rather, the reduction from those levels to 30 and 15 ppm, respectively. Based on observations in the European refining arena, the ultimate reality is probably zero sulfur in all fuels – a target that cannot be achieved economically using existing catalytic hydrotreating technology.

Trans Ionics Corporation, under SBIR grants from the Department of Energy, is developing a novel, non-catalytic process, called TransFining™, to effectively desulfurize liquids fuels to ultra low levels (<10 ppm S) at intermediate temperatures (~260°C) and low pressures (<300 psig H₂). Unlike conventional catalytic hydrotreating, TransFining™ also works well on fuel oil, vacuum residual oils and heavy crudes, making it an extremely flexible process. This paper will detail the results of recent experimental studies and preliminary economic analyses that show TransFining™ to be a more cost effective option than catalytic hydrotreating for low sulfur fuel oil and ultra low sulfur fuels.

1. Introduction

The production of ultra low sulfur (ULS) gasoline and diesel, at a cost that is sustainable long term and in quantities that will continue to meet the demands of U. S. drivers, is potentially the single most significant and costly challenge that will be faced by the refining industry during this decade. On one hand, sulfur in fuels is a known problem. It is not only directly responsible for increased levels of NO_x in exhaust gases; but it is also a poison for many of the newer catalytic converters that are being introduced by automakers. Paradoxically, supplies of crude oils are becoming increasingly heavier and more sour (higher sulfur levels) thus requiring more processing. As a result, refiners are already having to hydrotreat feeds more severely just to stay at the current sulfur levels.

Sulfur reduction in transportation fuels is primarily being driven by changes in governmental regulations worldwide. The U.S. and foreign governments have mandated scheduled reductions in sulfur for both gasoline and diesel, which many refiners will find difficult to meet. On December 21, 1999 the EPA issued its Tier 2 regulations requiring a reduction of sulfur in gasoline to an average of 30 ppm effective January 1, 2006. Diesel has been impacted to an even greater extent. On May 17, 2000, the EPA issued a Notice of Proposed Rulemaking calling for a 97% reduction in the maximum sulfur level in diesel (from 500 ppm to 15 ppm) effective June 2006. Since this is a maximum, realistically, this translates into an average of only 7-10 ppm S in diesel.

Considerable effort is being expended by refiners and other organizations to develop technology that will allow them to meet the mandated sulfur specifications on time. New lower pressure naphtha (gasoline) hydrotreating technology is being developed and capital funds are already being allocated to build additional higher pressure distillate hydrotreaters. In addition, new reactive distillation, adsorption and pervaporation-based membrane processes have also been announced. There is general agreement in the industry that the major hurdle is not the initial reduction of sulfur in gasoline to 120 ppm and diesel to 100 ppm but rather, the reduction from those levels to 30 and 15 ppm, respectively. Refiners today have basically two choices of technology for lowering the sulfur content of transportation fuels: (1) those based on hydrotreating and (2) those that are not. The applicability of these processes depends to a large extent on whether the feed stream is gasoline or diesel.

Trans Ionics Corporation of The Woodlands, TX has developed two processes for sulfur removal which fall into the non-hydrotreating category. TranSep™ is a patented membrane pervaporation process for removal of sulfur from gasoline boiling range feeds; and TransFinishing™ is a unique process that uses elemental sodium to remove sulfur from feeds ranging in boiling point from distillate to heavy oil and bitumen. This paper will focus on the development of TransFinishing™ for desulfurization of a range of feeds.

2. Background

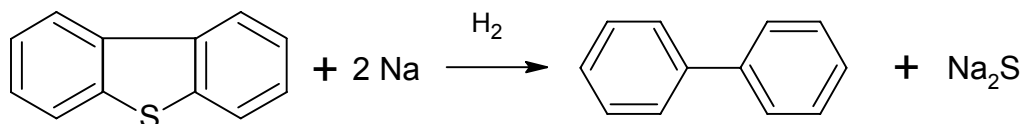
The use of sodium metal to treat feeds was first suggested and patented seventy-five years ago [Hofass 1929]. The procedure employed metallic sodium at medium pressure (>700 psig) hydrogen and elevated temperatures (> 575 °F). This was followed by work at Standard Oil of Indiana [Ruthruff 1933], DuPont [Vose 1934] and a major effort by Esso Research and Engineering Co. [Kimberlin 1963, Welty 1974, Bearden and Fink 1974, Baird and Bearden

1977 and Bearden 1978] in the mid 1970's investigating the effects of sodium treating on residual oil.

In addition to the extensive work done on heavy oil desulfurization, sufficient work has been done on naphtha and diesel streams to show that desulfurization using sodium is also possible. Earlier work also done at Esso [Vanderbilt 1957] demonstrated that sulfur in light cat naphtha (LCN) could be reduced from 210 ppm to 2 ppm using 1 wt. % Na at 410 °F. Later work at Exxon Research and Development Laboratories [Howard et al. 1977] also showed that 90% desulfurization of LCN could be achieved with **no loss in RON** (a feat which naphtha hydrotreating technology still cannot accomplish).

Similar results are achievable with distillate fuels. Sternberg and coworkers [Sternberg et al. 1974] showed that 99% of sulfur could be removed from dibenzothiophene (a molecule typically found in diesel) at 200 psig hydrogen pressure and 350 °C.

The chemistry of sodium treating to remove sulfur is straightforward as shown in the reaction below:



Because the sodium is a stoichiometric reagent and not a catalyst, it is consumed in the reaction producing one mole of Na₂S for every two moles of sodium consumed. More importantly, only one mole of hydrogen (H₂) is required for every mole of sulfur removed, leading to extremely low hydrogen consumption. Required pressure is low (< 300 psig) because it is simply necessary to have hydrogen available to stabilize the intermediates produced to keep them from undergoing recombination (which would produce a higher molecular weight product).

These data all show conclusively that heavy oils, naphtha and diesel can all be desulfurized under mild conditions by the use of alkali metals like sodium. So why then was this technology never commercialized? We believe the clear answer is economics. Even for trim desulfurization, the cost of sodium is too high to allow it to be used on a once-through basis (there is also a safety issue with the storage of large quantities of molten sodium and a further issue of recovering and disposing of the sodium sulfide product). In order to be economically viable, sodium must be regenerated and recycled to the feed. One way of achieving this was to use the sodium-sulfur battery developed by Ford Motor Company in 1969 just prior to the time this desulfurization work was being done in the mid 1970's. It was anticipated that Ford's battery research would result in an improved electrochemical cell that could economically and efficiently recover the sodium. Unfortunately this was not realized during that time; and the technology was never commercialized. Trans Ionics, however, has recently developed a novel and improved sodium sulfur battery that is the heart of its TransFining™ desulfurization process; and this paper is the first to describe both the process and technological innovations behind it.

3. The TransFining™ Process

TransFining™ has been in active development since early 2001 under the sponsorship of the U. S. Department of Energy. Since work done over the past thirty years has shown conclusively that sodium treating was capable of removing sulfur from a wide range of feeds, the primary focus of this work has been on the development of a new and improved sodium-sulfur battery to regenerate the active sodium reagent. A schematic of the overall process is shown in Figure 1.

In this process, feed is mixed with elemental sodium using a proprietary procedure and then passed through the desulfurization reactor. Experimental work has shown that the reaction takes place at temperatures above 260 °C (500 °F) and furthermore that the reaction is extremely rapid. This results in a finely dispersed Na₂S product which is separated from the desulfurized product in a proprietary separator and sent to the sodium-sulfur battery for processing. Sodium regenerated in this way is recycled to the feed stream and the other product (elemental sulfur) is recovered for disposal.

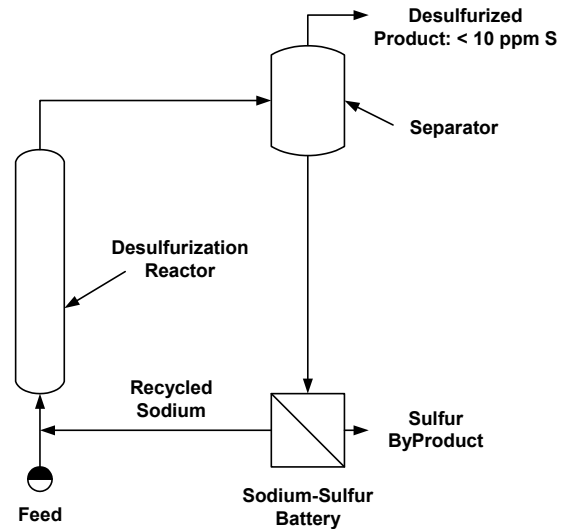


Figure 1. Schematic of TransFining™

4. Sodium Sulfur Battery

The basic construction of a sodium-sulfur battery is shown below in Figure 2. In this design the two electrodes are liquid (liquid sulfur and liquid sodium) rather than solid as is the case in lead-acid batteries. The battery must thus operate at temperatures above the melting points of these two materials and traditionally has been run around 350 °C (661 °F). Liquid sodium is electrically conductive and acts as its own electrode. Liquid sulfur, unfortunately, is not; and that compartment requires a conductive material such as graphite gauze (or the like) to carry current.

The electrolyte dividing the two electrodes is solid β" - Al₂O₃, which conducts only sodium ions. Because, in the typical battery applications developed in past years, the electrolyte was usually self supporting, it was constrained to be thick enough to resist breakage (which could produce the dangerous mixing of sodium and

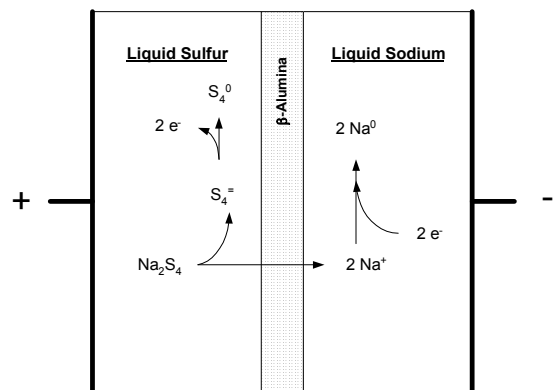


Figure 2. Sodium Sulfur Battery

sulfur). This means that electrolytes were normally 1-2 mm thick.

Under normal discharging conditions, sodium ions diffuse across the electrolyte and react with sulfur producing a complex mixture of sodium polysulfides and electricity at ~1.7 V. If a potential is applied instead, (charging mode at 2.1 V as shown in the drawing), the reaction is reversed, producing Na and S from sodium sulfide (which is the desired reaction for use in fuels desulfurization). Thus, this membrane, like all other membranes in which diffusion through the bulk is the rate-limiting step, would show marked improvement in sodium flux if the membrane electrolyte were significantly reduced in thickness.

The two major problems with sodium-sulfur batteries to date have been (1) their low power density (current per unit area expressed as A/cm^2) which is, in part, caused by the thickness of the electrolyte, and (2) their cost. Attempts to run at higher power densities in the past have resulted in a fractured β'' - Al_2O_3 membrane.

The first commercial application of these batteries for electric utility loading leveling was in Japan at the Kawasaki Substation of its Kawasaki Electric Energy Storage Facility; and this system has been in operation since the end of 1998. Unfortunately, it cost ¥1.5 billion for only 500 kW (about \$25,000/kW); and cost remains a major stumbling block to successful and widespread application of this technology.

5. Improved β'' - Al_2O_3 Electrolyte

The key to Trans Ionics' sodium sulfur battery is the electrolyte. As mentioned previously, whereas most β'' - Al_2O_3 electrolyte films made to date were relatively thick (800 – 2000 μ), the TransFining™ battery electrolyte is only 20 μ , a reduction of 40 to 100 over previous electrolytes. Since transport rate of sodium is inversely proportional to the film thickness, these films exhibit a higher transport rate than thicker films. An SEM photomicrograph of one of these films is shown in Figure 3. As can be seen, the electrolyte is fully dense (which is important since leakage of reactant through pinholes lowers the efficiency of the battery).

These films have been characterized by AC impedance spectroscopy and found to have conductivities equal to or better than those obtained by Ford Motor Company researchers who invented the sodium sulfur battery [Kummer and Weber 1971].

6. TransFining™ Economics

When viewed as an entire process, TransFining™ offers a number of significant advantages over conventional hydrotreating. The primary advantage is in capital and operating cost reduction. Since the process operates at < 300 psig and < 575 °F, there is no need for more expensive high temperature, higher pressure vessels. Secondly, since the

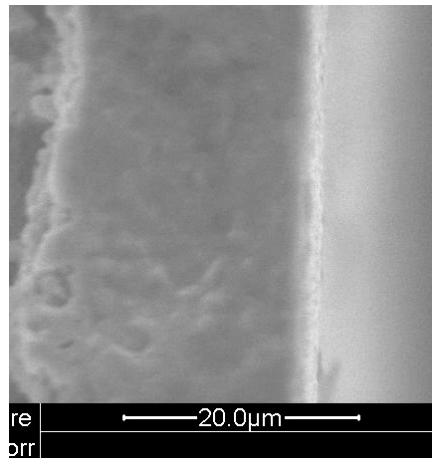


Figure 3. SEM Cross Section of Electrolyte

desulfurization reaction is extremely fast, the size of the primary reactor is reduced significantly. Residence times of 5 – 10 minutes are anticipated for complete conversion. Third, because the battery has a high efficiency, it is anticipated to be manufactured for a fraction of the cost of the Japanese batteries.

Operating cost reduction is also realized. Hydrogen consumption is only 1% of that used in conventional hydrotreating. With operation at lower temperatures and pressures, energy consumption is also significantly reduced.

A confidential study comparing TransFining™ to conventional hydrotreating for reduction of sulfur in an atmospheric residuum from 3.8 wt% to 0.1 wt% showed that the capital costs and annual operating costs were 38% and 35%, respectively, of conventional hydrotreating - a substantial reduction in both. Because of these attractive economic figures, TransFining™ is expected to find application in both refining operations for distillate, VGO and fuel oil desulfurization as well as in upstream heavy oil/bitumen upgrading in Canada and Venezuela. Trans Ionics Corporation anticipates having TransFining™ available for commercial sale in mid 2007.

Acknowledgements

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