Residue Value-Upgrade Opportunities From MSAR® Fuel Technology

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Abstract

A number of leading oil companies including Exxon, BP, Shell, Total and Petrobras have given consideration to manufacture of oil-in-water emulsion fuel from heavy refinery residues as a means of enhancing refining margins. The margin enhancement arises from recovery to the fuel pool of high value cutter stock added to residue to meet heavy fuel oil viscosity specifications and make a transportable fuel oil product.

Last summer a commercial demonstration of MSAR® (Multiphase Superfine Atomised Residue) technology was successfully completed at AB Mazeikiu Nafta’s 200 000 BPD refinery in Lithuania. Over 140,000 barrels (22,000mt) of MSAR® fuel was manufactured in a joint initiative between the refinery, Quadrise Fuels International plc (QFI) and its technology licensor AkzoNobel. The MSAR® was subsequently transported over 300km by rail and combusted at the 1800MWe Elektrenai power plant owned by AB Lietuvos Elektrine.

The commercial demonstration established the technical and commercial viability of MSAR® technology in an operating refinery environment, and opens opportunities for refiners to add significant value to residue streams without incurring the high capital costs and extended schedules associated with conventional hydrogen addition or carbon rejection upgrading technologies.

This paper provides an overview of the MSAR® solution, its fit with refinery upgrading options and the results of refinery manufacture, handling and combustion in a base-load supercritical boiler; providing a competitive alternative to natural gas.

Introduction

Commencing 1990 British Petroleum (BP) and Petroleos de Venezuela (PDVSA) successfully established a 6.5 million tpa market for their proprietary emulsion fuel Orimulsion® – a 70% bitumen in 30% water emulsion. The product, manufactured from 8° API Orinoco bitumen, was exported world-wide as a boiler fuel for power generation.

By 2003 supply contracts with major gencos had been secured for power plants in North and Central America, Europe and Asia. A US Environmental Protection Agency report had established that under adequate safeguards Orimulsion® could comply with all environmental legislation; and the technical success of Orimulsion® for a 160MWe Wärtsilä
A diesel generator plant in Guatemala had opened new horizons for application of the fuel. By 2006 over 60 million tonnes of the Orimulsion® had been shipped to customers worldwide.

PDVSA did not capitalise on this commercial success however. Orimulsion® became the target of an unprecedented domestic attack carried out through the public media by both the Minister of Energy and the new PDVSA president appointed by Hugo Chavez. The final blow was for PDVSA to renge on its long-term supply commitments¹. Production of the product ceased in December 2006.

In parallel to the Orimulsion® development, a group of former BP experts were developing a low-cost emulsion technology alternative to Orimulsion®. In conjunction with AkzoNobel, modular licensed technology was developed that led to the MSAR® fuel solution. The MSAR® solution differs from Orimulsion® in that it is applicable to refinery residues as well as extra-heavy crudes, and is scaleable to lower throughputs than the Orimulsion® process. On-site refinery emulsion fuel manufacture is now an economically viable proposition utilising difficult to dispose of residues.

QFI and AkzoNobel (AN) have a strategic alliance to jointly implement MSAR® technology, principally seeking to add value through the refinery residue feedstock option. QFI acts as a sink for residues which are purchased by QFI at a price above their intrinsic value. These are then processed to emulsion fuel in a QFI owned facility on a BOO basis and sold globally to energy consumers equipped with flue gas desulphurisation facilities. The technology is also available to refiners under licence from QFI/AkzoNobel.
The MSAR® solution for refiners

From a refiner’s perspective, MSAR® offers a solution to the dilemma surrounding HFO production: HFO is sold at a discount to crude, consuming valuable diluents (used to reduce the viscosity and density of oil residues) and thereby reducing profitability.

The ‘value add’ of MSAR® over HFO production is that no diluents are needed to produce a transportable fuel with similar physical properties. This advantage increases with heavier crudes or more severe refining conditions.

Extra-heavy refinery residue is mixed with water and a surfactant package in a colloid mill to produce a stable emulsion fuel that behaves like a heavy fuel oil (HFO).

The MSAR® solution can be integrated into existing refinery and HFO infrastructure (Fig.1). Hot residue is slip-streamed (or the whole stream is diverted) from the residue run-down system after maximum process heat has been recovered, but before expensive cutter stock is added (Fig.2).

![Fig.1 – Conventional HFO production](image1)

![Fig.2 – MSAR® integration into HFO systems](image2)

The refiner is thus provided with a modular, low-capex, short-lead uplift pathway. The MSAR® option is especially relevant in today’s climate of high project costs and extended delivery schedules which increase risk and negatively impact conventional upgrading processes. The capex is low enough for MSAR® also to be considered as an interim value adding residue disposal solution pending the planning, approval, financing and implementation of major upgrading schemes.

MSAR® technology leverages equipment perfected over 20 years for road emulsion application. MSAR® systems can be installed within 6-12 months, utilising existing fuel oil infrastructure. Over 100 emulsion production modules have been supplied by AkzoNobel since 1980.
Water for the emulsification process can be derived from a number of sources including natural reserves, standard utility water, oil-contaminated waste water or sour water streams.

**Lithuanian commercial demonstration of MSAR® technology**

**The background**

The first large-scale commercial demonstration of MSAR® technology involved the alignment of an MSAR® production facility on the 200 000 BPD Mazeikiai refinery with the Elektrenai super-critical steam cycle power plant.

Mažeikiai refinery is 90% owned by PKN Orlen through its subsidiary AB Mazeikiu Nafta (MN), with the remaining 10% owned by the Lithuanian Government.

AB Lietuvos Elektrinė (LE) owns the 1800 MWe thermal power plant situated less than one hour’s drive west of Vilnius. The plant consumed Orimulsion® for over a decade up to 2004, when supplies were unilaterally terminated by PDVSA.

**Mažeikių Nafta refinery integration of MSAR®**

Integration options for MSAR® technology were reviewed with the refinery in the context of their future re-configuration plans. It became apparent that there was significant potential for MSAR® to add value around the existing visbreaker and that this could be substantially enhanced by addition of a low capex vacuum flasher unit.

**Operational enhancement**

Severity of Visbreaker operation is limited by the stability requirement of the final finished blended fuel oil and the extent of fouling and coke laydown in the visbreaker heater. The former requirement means that the stability of the residue must be sufficient to ensure that the finished fuel, resulting from blending with diluents that are less aromatic than the residue, is stable and that the asphaltene content does not flocculate out.

Where the residue is made into MSAR®, stability is not an issue and severity may be increased, subject to acceptable levels of heater fouling and coke deposition.

Some operational modifications, such as increasing steam injection or re-cycling heavy distillates from the visbreaker fractionator, may help mitigate coking tendency while some relatively low-cost options to increase heater capacity might be
implemented in certain instances. In the absence of any other constraint, a limit on residue stability is recommended (in terms of the Shell p-value test, equivalent to a p-value of 1.05).

Addition of a vacuum flasher to recover a major part of the visbroken vacuum gasoil (VVGO) for use as additional cracker feed further enhances the yield of higher value products.

After review Mazeikiu Nafta decided on use of a higher severity visbreaker operation and addition of a vacuum flasher integrated with MSAR® production and configured as below:

**Fig.3 – MSAR® integration at Mažeikių Nafta**

**Legend:**
- Current crude -> HSFO flow scheme
- Flow scheme for MSAR® demonstration
- Planned future configuration
- Future configuration incorporating MSAR®

**MSAR® commercial demonstration**

Early in 2008 commercial agreements were reached with both the refinery and the power plant to carry out a demonstration of MSAR® technology. 20,000 tonnes (125,000 barrels) of MSAR® were to be manufactured at the refinery for supply to the power plant via the state railway, AB Lietuvos Geležinkeliai (LG). Binding agreements for MSAR® off-take, refinery services, MSAR® supply, and 3rd party provision of support resources were put in place. QFI financed and managed the MSAR® installation and operations, and were buyer and seller of the refinery residue and MSAR® fuel respectively.

A temporary MSAR® production facility was installed within the MN refinery compound, using an existing plot area of less than 250m². The main equipment items consisted of a 20t/h MSAR® manufacturing unit (MMU), and five temporary 25m³ isotanks, to provide bulk emulsifier chemicals storage, buffer storage for residue feed, buffer storage for the MSAR® product and temporary storage for test batches of product. Buffer storage for water was provided by MN. MSAR® product pumps were installed to transfer the product to an existing HFO storage tank.
Utilities for the manufacture of MSAR® were supplied from the refinery systems, including:

- LP steam for heat tracing of the residue, emulsifier and water for start-up purposes
- River water for emulsion manufacture
- Cooling medium for residue
- Water for safety showers
- Electric power for the temporary MSAR® manufacturing facility (<100kW, 400V supply)

MSAR® product was pumped to a 12,600m³ fixed roof HFO tank (RZ-11) and stored between 33°C and 45°C before being exported by rail. Prior to commencement of MSAR® production RZ-11 was stripped of HFO, to minimise contamination of the MSAR®. The steam tracing on the existing rundown pipelines was turned off during MSAR® service.

MSAR® export was by rail using the refinery HFO rail loading system. Normally, HFO is stored in four storage tanks which are manifolded to allow either of 2 black oil export pumps to take suction from any HFO tank. The refinery's standard rail loading procedures were therefore modified by QFI to minimise product contamination and physical damage to the emulsion during the demonstration. Trains of 50 wagons each were loaded in 60t (nominal) rail wagons. In total 8 trains were loaded and over 20,000t of MSAR® exported from the refinery to the LE power plant (ca. 300km). The same discharge system used for HFO offloading was deployed for MSAR®. Unlike HFO, no steam heating was required for MSAR® offloading due to the low viscosity of the product at the delivery temperature of 35-40°C.

The schedule for commissioning, production and combustion of MSAR® is summarised below. Once the initial commissioning tests were completed (including test batch pumping and handling tests) production of MSAR® began on a continuous basis. Production of the MSAR® demonstration volume (nominally 20,000 tonnes) began at the end of June, and was completed early September. Commissioning of the power station systems on MSAR® took place mid-July (with a break in production), with base load operations scheduled for two weeks during September:

MSAR® product was formulated to maintain fuel quality specifications during recommended storage and handling for 3 months. In order to provide comprehensive Quality Control and
Quality Assurance (QC/QA), a regime of regular laboratory testing was undertaken to constantly monitor the quality of the MSAR® produced, stored, transported and delivered, and to ensure that any issues relating to the formulation and/or specification of the emulsion fuel were detected early, so that any required remedial action or adjustments to the manufacturing process could be taken. Dedicated laboratory facilities were set up on the MN site by QFI and AkzoNobel. An overview of MSAR® demonstration sampling is summarised below:

**MSAR® production and operating experience**

There is a significant difference between formulating an oil-in-water emulsion in a laboratory and producing a commercial batch of the fuel. The inventory value at commercial risk through the supply chain equates to several million dollars. The QFI team deployed for the demonstration has over 40 years of combined emulsion fuel operational experience, which together with the skills sets provided by Alliance partner AkzoNobel sets QFI aside from potential competitors in emulsion fuels.

A series of commissioning tests were undertaken to simulate handling conditions expected during the demonstration, including; pumping, storage and HFO cross-contamination tests.
Based on results during commissioning, the formulation of MSAR® for the commercial demonstration was determined. During the demonstration the viscosity of the supplied visbreaker residue varied between 300 – 700 cSt (at 100°C), with the refinery processing predominantly Urals-derived crude or 50/50 blends of Urals with heavy North Sea crudes.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Expected Quality</th>
<th>Contractual Specification</th>
<th>Analytical Method or Equipment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinematic Viscosity, cSt (at 100°C)</td>
<td>1300</td>
<td>1750 Max</td>
<td>GOST 33 (or similar)</td>
</tr>
<tr>
<td>Density, kg/m³ at 20°C</td>
<td>1.04</td>
<td>1.05 Max</td>
<td>GOST 3900</td>
</tr>
<tr>
<td>Sulphur, % w/w</td>
<td>2.5</td>
<td>3.5 Max</td>
<td>GOST 1437 (ASTM D-4294)</td>
</tr>
<tr>
<td>Ash, % w/w</td>
<td>0.1</td>
<td>0.2 Max</td>
<td>GOST 1461</td>
</tr>
<tr>
<td>Net Calorific Value, MJ/kg</td>
<td>39.5</td>
<td>39.0 Min</td>
<td>GOST 21261</td>
</tr>
</tbody>
</table>

It was observed that the viscosity of the residue had a direct effect on the MSAR® production viscosity (Fig. 5), this was compensated for by minor adjustments in the MSAR® manufacturing parameters.

Fig. 5: Variation in MSAR® viscosity during production

Besides these adjustments for viscosity control, all other parameters (in terms of MSAR® droplet size characteristics, determined stability, etc) remained within expectations and specification, demonstrating the stability and reliability of the process and resulting fuel. The specification of the delivered MSAR® to the client was designed to be similar to Orimulsion® with average results summarised below based on independent inspection:
Characteristics:

<table>
<thead>
<tr>
<th>Orimulsion® (400 Spec.)</th>
<th>MSAR® (Urals VBR)</th>
<th>Analytical Method or Equipment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Content, % w/w</td>
<td>30</td>
<td>ASTM D-4006</td>
</tr>
<tr>
<td>Mean droplet Size, Microns</td>
<td>20</td>
<td>Malvern Particle Sizer</td>
</tr>
<tr>
<td>Droplets &gt; 150 Microns, % w/w</td>
<td>0.5</td>
<td>Sieve Test</td>
</tr>
<tr>
<td>Apparent Viscosity @ 20s⁻¹, cP</td>
<td>200 @ 30°C</td>
<td>Coaxial Cylinder Viscometer</td>
</tr>
<tr>
<td>Gross Calorific Value, MJ/Kg</td>
<td>30</td>
<td>ASTM D-240</td>
</tr>
<tr>
<td>Net Calorific Value, MJ/Kg</td>
<td>28</td>
<td>ASTM D-240, Calculated</td>
</tr>
<tr>
<td>Sulphur, % w/w</td>
<td>2.8</td>
<td>ASTM D-1552</td>
</tr>
<tr>
<td>Sodium, ppm</td>
<td>10</td>
<td>Atomic Absorption</td>
</tr>
<tr>
<td>Vanadium, ppm</td>
<td>320</td>
<td>Atomic Absorption</td>
</tr>
<tr>
<td>Nickel, ppm</td>
<td>70</td>
<td>Atomic Absorption</td>
</tr>
<tr>
<td>Magnesium, ppm</td>
<td>5</td>
<td>Atomic Absorption</td>
</tr>
<tr>
<td>Ash, % w/w</td>
<td>0.10</td>
<td>ASTM D-482</td>
</tr>
</tbody>
</table>

The quality of MSAR® in storage was closely monitored (See Fig.6). Through progressive adjustments in the MSAR® formulation, quality parameters remained constant during the site storage of MSAR® demonstrating the high stability of the fuel over time.

Fig. 6: Variation in MSAR® oil droplet size in refinery storage

MSAR® Combustion

MSAR® was fired at the power plant on the 2x150MWe Unit 7. The Russian-designed boilers consist of two opposed-wall fired 150MWe boilers each with six burners, supplying 950 t/h 240bar steam (540°C reheat) to a single Russian LMZ turbine. Unit 7 is installed with pollution abatement systems to meet EU new plant standards.

The objectives of the MSAR® combustion demonstration programme were:

- Establishing operational suitability of LE fuel handling system with MSAR®
- Establishing optimised combustion emissions within legislative compliance
- Establish maximum sustainable load on Unit 7
- Determine any operational limitations when firing MSAR® on Unit 7
- Establish efficiency when firing MSAR® on Unit 7
Initial test-firing of MSAR® was undertaken during July, but the main period of combustion test firing took place between 08th to 19th September. The aim during this period was to progressively migrate from firing natural gas to 100% MSAR®, and then to optimise performance while firing the emulsion fuel.

The highest load achieved during the limited MSAR® firing period represented about 75% of maximum load. This was not due to any impact relating to the combustion of MSAR®, but due to under-sizing of the mass flow meters fitted on both Unit 7 boilers (resulting in a high oil pressure drop across the devices). MSAR® firing proved extremely satisfactory; achieving flame stability at both low and high load operations. Part way through the firing programme, LE undertook a visual inspection of the boiler internals and concluded that the levels of fouling were acceptable and within expectations.

Overall MSAR® emulsion fuel was fired under fully compliant conditions when the flue gas abatement equipment was in operation; and met all expectations. It was concluded that additional optimisation when firing MSAR® would likely further improve the combustion performance on the Unit. This is tentatively scheduled for later in 2009.

Conclusions

Overall it can be concluded that the MSAR® commercial demonstration was a success for all the parties concerned. The main objectives met from the demonstration were that:

- an MSAR® production system could be integrated within the refinery environment, to produce commercial volumes of fuel.
- the MSAR® production system could be operated on a continuous 24/7 basis without significant unforced outage periods.
- MSAR® fuel from visbreaker residue derived from Urals crude (or a Urals blend) was a stable product, meeting all the end-user technical and commercial requirements.
- MSAR® fuel could be produced and exported from the refinery alongside conventional HFO on a campaign basis, using the existing infrastructure and transport systems.
- MSAR® fuel performance was acceptable, and deemed by the client to be similar to, or better, than Orimulsion®.

Commercial discussions are ongoing between the parties to conclude agreements for the commercial MSAR® facilities required to provide an economic base-load energy alternative for the Elektrenai plant from 4Q 2009.
Testimonials

Public testimonials and recognition from the commercial demonstration are summarised below, with further details available from the respective company’s websites:

“Results of emulsified fuel trial test are excellent”
http://www.nafta.lt/en/

“The MSAR® commercial demonstration has confirmed to us that the technology offers a commercially viable alternative to fuel oil production, and has a suitable fit with future plans for our refinery.”
General Director – AB Mazeikiu Nafta

“Use of QFI’s MSAR® emulsion fuel at our Elektrenai plant has demonstrated the fuel is comparable with Venezuelan Orimulsion® and is suitable for long-term operation in those of our units installed with our new air pollution control equipment. From 2009 onwards MSAR® could offer us a competitively priced Lithuanian sourced fuel as an economic alternative to our current supplies”
General Director – AB Lietuvos Elektrine (1800MWe)

“AB Mažeikių Nafta Product Awarded Gold Medal” (2008.12.18)

Today in Vilnius City Hall, the President of the Republic of Lithuania Voldas Adamkus has awarded the General Director of AB Mažeikių Nafta Marek Mroczkowski with the gold medal for the Lithuanian Product of the Year. The Company was given the top award of the Lithuanian Confederation of Industrialists for the emulsified fuel.

The Company’s newest product, created by the specialists of AB Mažeikių Nafta and Quadrise Fuels International, was produced and successfully tested in Lietuvos Elektrinė company this year in summer. “We are proud of such high recognition of the work of our Company’s specialists, — said M. Mroczkowski. — We hope that our product will contribute to reduction of dependence on gas and, because of its price, it will be a good alternative to heavy fuel oil.”

http://www.nafta.lt/en

References

1 Oil & Gas Journal, September 22, 2008 volume 106, issue 36
2 Predominantly for bitumen-emulsion service for road applications