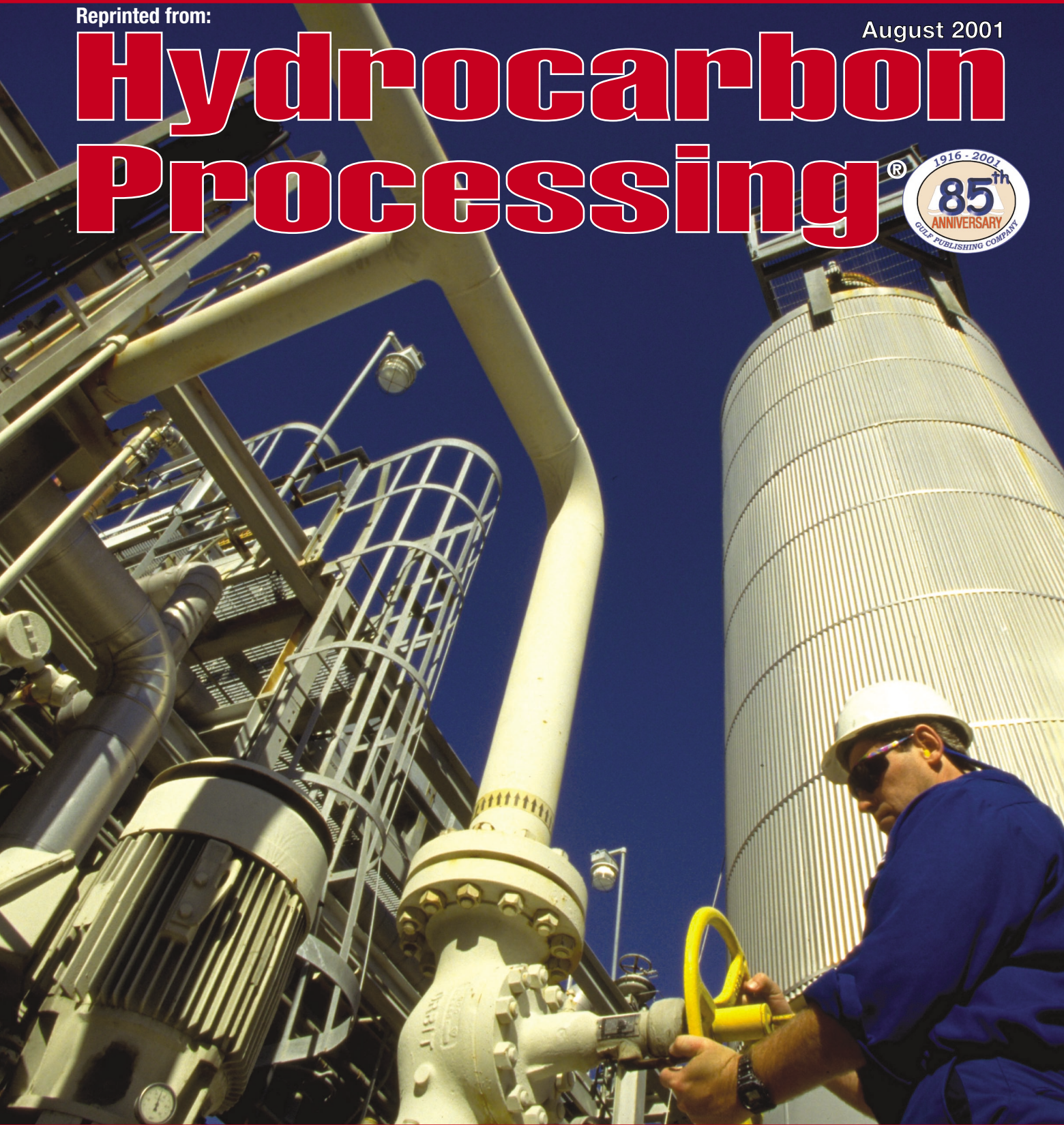


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Improve haze removal for FCC gasoline

This refinery used advanced coalescer techniques to separate very stable emulsions and dispersions by mechanical means

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C caustic carryover from a treater can cause downstream contamination of fluid catalytic cracked (FCC) gasoline; **Result:** off-specification product. Caustic forms a very stable emulsion with gasoline that results in high levels of sodium, water and phenols in the final product. New developments in coalescing technology have made it possible to separate very stable emulsions and dispersions.

In the following case history, the Mol-RT's Szazhalombatta Refinery experienced emulsion problems from caustic carryover. Eager to resolve this condition, refinery engineers investigated several technologies to break the emulsion and mitigate the problem. One option considered was a new high-efficiency fluoropolymeric liquid/liquid coalescer to optimize the caustic treating system. This case history details the benefits when using present and new separation equipment to control gasoline emulsion problems.

Caustic problems. The Mol-RT Refinery in Szazhalombatta, Hungary, operates a caustic-treating unit to remove mercaptans from FCC gasoline. This unit processes 130 m³/h (19,624 bpd) of FCC gasoline. In this process, FCC gasoline is delivered to two fixed-bed reactors, each containing a catalyst impregnated onto an activated carbon substrate. Cobalt and vanadium pthalocyanines are used as catalysts due to their high activity and stability in the oxidation reaction for mercaptans and low solubility in petroleum fuels.¹ Caustic (3° Baumé) and oxidizing air are injected into the FCC gasoline upstream of the reactor. In the reactor,

mercaptans are extracted into the caustic and then converted to disulfide oils by oxidation and catalytic action. Also, phenols are extracted into the caustic phase. The reactor effluent flows to a three-phase separator where air, disulfides and regenerated caustic are separated. Regenerated caustic is recycled back to the reactor. Fig. 1 shows a simplified schematic of the caustic-treating unit. The process parameters for the Mol-RT Refinery caustic treater are presented in Table 1.

The reactor effluent contained a quantity of carried-over caustic that resulted in hazy gasoline product, high costs for caustic makeup and corrosion of downstream piping. However, the hazy gasoline was problematic. It had to be blended off or reprocessed; otherwise, it would cause the final product to be off-specification for sodium. Likewise, the carry-over caustic could also react with methyl tertiary butyl ether (MTBE) that was blended into the gasoline downstream of the caustic-treating system.

SEPARATION OPTIONS

To reduce the caustic excursions downstream of the treating unit, Mol-RT considered several options, which include settling tanks, mesh-pad beds, electrostatic separators, sand beds and water washing:

Settling tanks were deemed not viable due to the high stability of the caustic-fuel emulsion. A stable emulsion contains very small droplets that do not settle efficiently, and excessive settling time and/or tank volume would be required.

Mesh pads operate by the principle of inertial impaction whereby the droplet momentum is great enough so the droplet leaves the streamlines of the fluid flow and impacts metal fibers or plates in the mesh pads. These droplets then coalesce into large drops that separate by gravity. Mesh pads do not work well when the

Table 1. Caustic treater process parameters.

Application	Removal of caustic from gasoline
Process flowrate	130 m ³ /h (19,624 bpd)
Temperature	40°C (104°F)
Pressure	6.5 barg (94.3 psig)
Gasoline viscosity	0.55 centistokes @ 38°C
Gasoline density	0.68 g/ml
Caustic density	1.02 g/ml
Interfacial tension	12.4 dyne/cm
Caustic water pH	12.4
Total suspended solids	< 1 ppmw
Injected caustic concentration	3° Baumé (2.3 % wt)

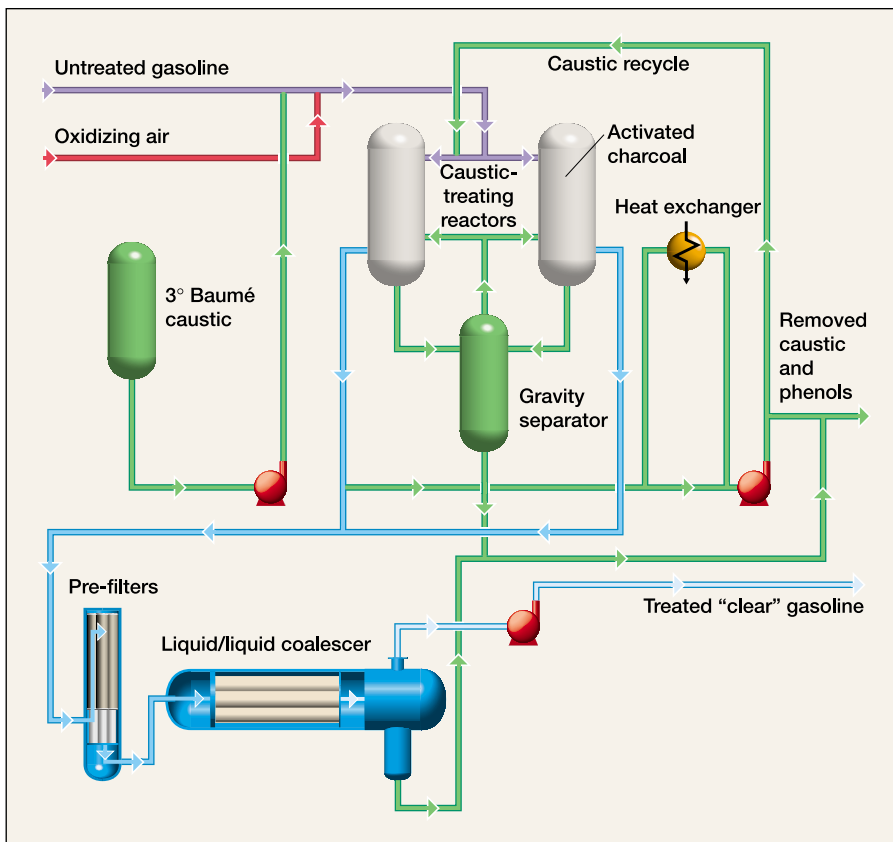


Fig. 1. Caustic treating Unit at the Mol-RT Refinery.

carbon fuels by acting as coalescers whereby the small caustic droplets adsorb onto the sand and form larger drops that are also separated by gravity. In practice, however, sand beds are prone to severe problems of fluid channeling through the bed caused by bed compaction and cracking. This often leads to poor sand bed performance and high manpower costs to load and unload the bed.

Water washing usually requires large extraction towers that have a high initial capital expense and additional separation equipment to remove any carryover water from the extraction process. This process consumes water that will require disposal or further treatment for re-use after the extraction process.

Liquid/liquid coalescers have the same low operating costs regardless of the amount of water or caustic charged to the unit. Based on the superior efficiency and low cost of separation, the Mol-RT Refinery decided to run field trials with high-efficiency polymeric liquid/liquid (L/L) coalescers.

Table 2. Caustic-fuel interfacial tension data gathered from field tests.

Plant location	Hydrocarbon	Interfacial tension, dyne/cm
U.S. Pacific	Heavy catalytic cracked (HCC) gasoline	0.7
U.S. Pacific	Light catalytic cracked (LCC) gasoline	0.6
U.S. Midwest	Heavy catalytic cracked (HCC) gasoline	0.5
U.S. Gulf Coast	Fluid catalytic cracked (FCC) gasoline	5.0
U.S. Gulf Coast	Light gas oil (LGO)	3.9
U.S. Gulf Coast	Heavy catalytic naphtha (HCN)	4.3
Canada	Refined oil (RO)	3.6-4.7
Canada	Heavy catalytic naphtha (HCN)	0.8
Canada	Light catalytic naphtha (LCN)	10.2
Canada	Kerosine	2.4
Singapore	Kerosine	8.4
England	Fluid catalytic cracked (FCC) gasoline	12.0
Hungary	Fluid catalytic cracked (FCC) gasoline	12.4

interfacial tension is low (< 20 dyne/cm) and the droplets are very small leading to poor droplet capture efficiency. Also at flowrates reduced from the original design, the inertial separation force is greatly lowered leading to poor separation.

Electrostatic precipitators separate caustic water from hydrocarbons by mean of an electric charge created by a high voltage source. While electrostatic separators can be effective, they require a high operating cost for electricity. Furthermore, they require significant initial capital expenditures and can have high maintenance costs when electrodes short circuit due to caustic slugs (increased conductivity) or scale buildup on the electrodes.

Sand beds are able to separate caustic from hydro-

L/L coalescer system. The traditional L/L coalescers have used glass-fiber media, which work well for emulsions that have interfacial tensions greater than 20 dyne/cm and for systems that have neutral water as the dispersed phase. New coalescer media, constructed with novel formulated polymers and fluoropolymers, are effective for emulsions having interfacial tensions as low as 0.5 dyne/cm and for harsh chemical environments such as the caustic/fuel system.^{2,3} High-efficiency polymeric coalescer have produced clean petroleum fuels with sodium levels below 0.5 mg/l and free water concentrations of < 15 ppmv.

A high-efficiency L/L coalescer in the horizontal configuration is shown in Fig. 2. The system consists of a pre-filter section followed by a horizontal coalescer cartridge stage with a settling zone that relies on the difference in density for separation of the coalesced droplets. The fluid enters at the side of the housing and flows from the inside of the coalescer cartridges radially outward causing the enlargement or coalescing of the inlet dispersion into large droplets in the outlet stream. These coalesced droplets then flow axially in the horizontal direction through a settling zone. The dispersed caustic-phase coalesced droplets settle downward by gravity and are collected in a sump located at the bottom of the housing. Purified gasoline leaves at the top of the housing.

The L/L coalescing system operates in three stages: separation of solids, coalescence and separation of coalesced drops:

Separation of solids. Solids can increase the stability of an emulsion; consequently, removing solids can make coalescing easier. Generally, this step can be achieved by a separate cartridge filter system or by a re-generable backwash filter system for high levels of solids. In addition, the filtration stage protects the coalescer and increases service life.

Coalescence. The next step is primary coalescence. In this stage, the pore dimensions begin with a very fine structure and then become more open to allow for void space for the coalescing droplets. In the primary coalescence zone, the inlet droplet dispersion containing fine droplets in the size range of 0.2 to 50 microns (μm) is transformed into a suspension of enlarged droplets in the size range of 500 to 5,000 μm .

The coalescence mechanism involves the adsorption of droplets to the coalescer fibers, followed by translation along the fibers and collisions at the junctures between fibers. In these collisions, the droplets merge together or coalesce.

The viscous drag of the bulk fluid stream then causes the enlarged drops to disengage from the fibers. This process is repeated a number of times through the coalescer depth until the large coalesced drops exit the coalescer media. The necessary condition that droplet-fiber adsorption occur for coalescing has been supported by many sources.^{4,5}

Separation of coalesced droplets. Once the droplets have been coalesced, they are now assumed to be as large as possible for given flow conditions. Separation is achieved by using a settling zone, which relies on the difference in densities between the coalesced droplets and bulk fluid. Caustic is separated in a collection sump that can be manually drained on a periodic basis or equipped with an automatic level control and drain system. Estimation of the coalesced drop size and required settling zone is best determined through pilot-scale tests at field conditions.

Surfactants. They are naturally present in crude oil, and thus, are found in refined petroleum products. During the oxidation process and the caustic recirculation in the sulfur-removal process, surfactants can be concentrated to high levels. Surfactants present in caustic treaters include: sulfides, mercaptides, naphthenic acids, cresylic acids and phenol homologs.⁶ Petroleum naphtha sulfonates have also been identified as natural occurring petroleum surfactants that are especially detrimental to glass-fiber conventional coalescers.⁷ The surfactants can adsorb at the solid/liq-

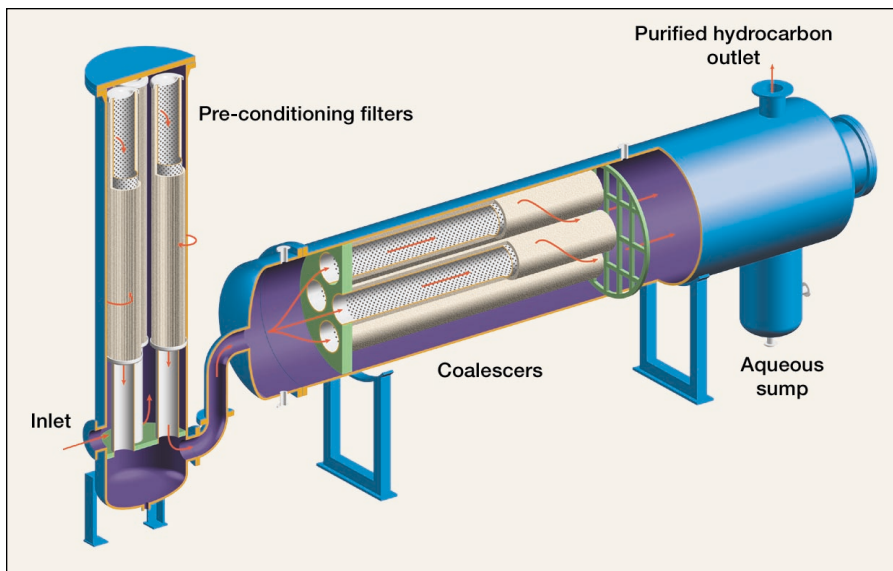


Fig. 2. High-efficiency L/L coalescer system.

Table 3. Pilot-scale L/L coalescer results.

Flowrate, lpm	Test duration, min	Volume of caustic water coalesced, liters	Visual appearance, inlet/outlet	Concentration of caustic solution coalesced, ppmv	Caustic water recovered, liters caustic water/m ³ gasoline
5	50	0.74	Hazy/Clear	3,000	3.00
11	115	4.00	Hazy/Clear	3,162	3.16
20	120	7.15	Hazy/Clear	2,979	2.98
23	1,405	64.63	Hazy/Clear	2,000	2.00

uid interface (coalescer fibers) or at the liquid/liquid interface (water/oil).

When surfactants concentrate on the coalescer fibers, this is known as “disarming.” The coalescer fibers are shielded from the passing aqueous droplets; this results in poor separation efficiency. Generally, the disarming phenomenon does not occur unless the interfacial tension between water and fuel is less than 20 dyne/cm. When specially formulated polymeric coalescer medium was used in place of glass fiber, disarming was not observed.^{2,3} The coalescing performance of a polymeric medium can be greatly enhanced by modifying surface properties that can not be done with glass-fiber medium.

Surfactants can also concentrate at the water/fuel interface. This condition can lead to very small droplets and stable emulsions. To separate these types of emulsions, special consideration must be directed to the pore size and distribution in the coalescer media to intercept and coalesce these fine droplets. Field tests conducted at caustic-treating units have uncovered similar results showing very low interfacial tension of caustic-hydrocarbon emulsions as shown in Table 2.

Pilot-scale L/L coalescer test. To evaluate the sizing and performance of the new fluoropolymeric coalescer to separate the carried-over caustic from the FCC gasoline at the sulfur-removal system outlet, a pilot-scale test coalescer unit was used at the Mol-RT

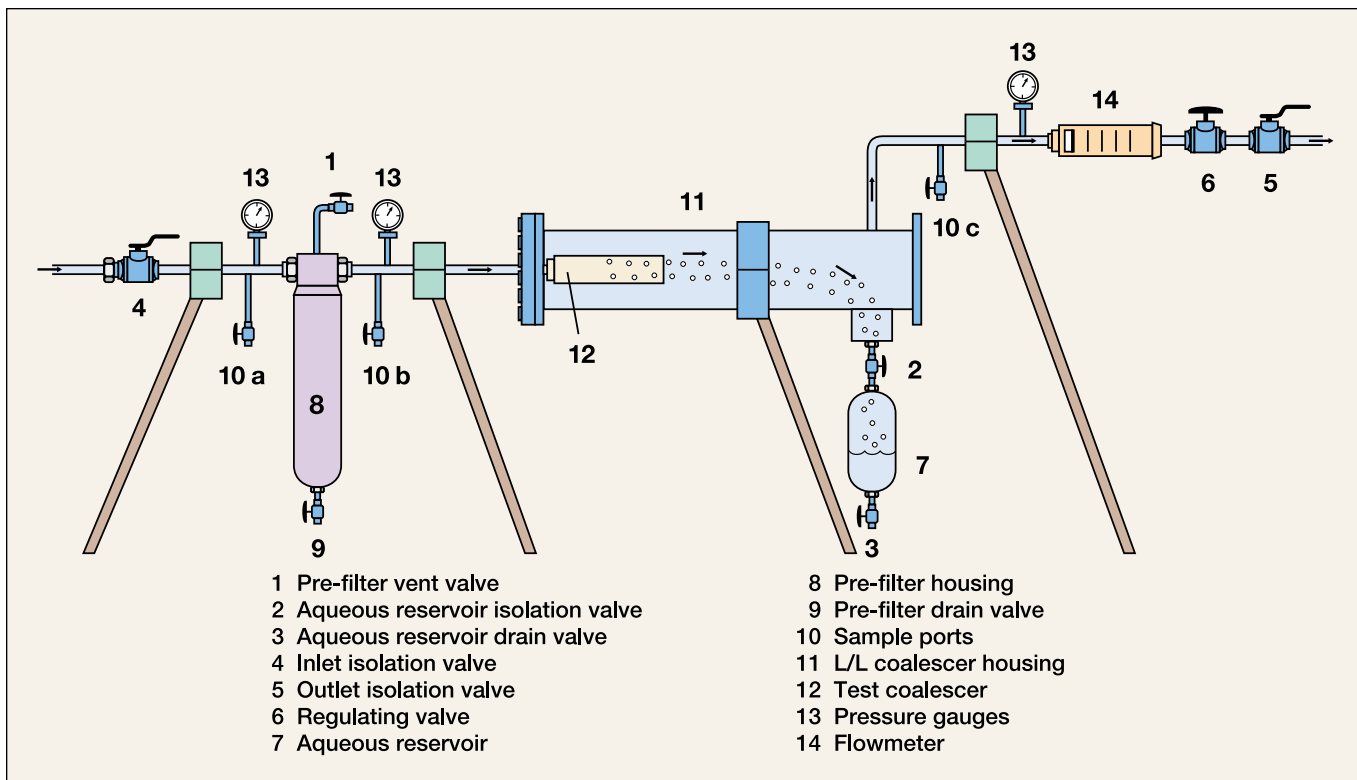


Fig. 3. Schematic of the pilot-scale L/L coalescer test unit.

Refinery. As shown in Fig. 3, it contained one 6-in. (152.4-mm) length high-efficiency liquid/liquid test coalescer and one 10-in. (254-mm) length pre-filter.

A slipstream was sent through the test unit, and the quality of the influent and the effluent was analyzed. If the effluent quality was acceptable, then the flow through the unit was increased and the fluid quality again analyzed. The flow through the test unit was increased until the effluent quality was unacceptable. In this case, the test was based on visual observations; as long as the effluent was "bright and clear," then the flowrate was increased. The results of the testing are summarized in Table 3.

In analyzing the data, the maximum flow that was run through the test unit was 23 lpm (6.1 gpm). A Karl Fischer total water analysis was conducted by Mol-RT Refinery; results showed that the gasoline at the outlet of the test coalescer had less than 15 ppmv of free water. The water concentrations measured were close to the water saturation value (251 ppmw @40°C) at the test flowrate of 23 lpm. It was also found that when the gasoline from the coalescer outlet was cooled to 5°C, it remained clear. The amount of caustic water collected by the test coalescer was 2 liters of caustic solution per m³ of gasoline (2,000 ppmv).

Data showed that the caustic/FCC-gasoline emulsion was a highly stable as indicated by the interfacial tension measurement of 12.4 dyne/cm. Any emulsion with an interfacial tension of less than 20 dyne/cm is considered very stable and difficult to separate using, settling tanks, mesh pads, sand beds or conventional glass-fiber coalescers. Based on the results from the field tests at Mol-RT Refinery, the installation of high-efficiency fluoropolymeric liquid/liquid

(L/L) coalescers was recommended. The coalescer would be intended to:

- Produce consistent "bright and clear" gasoline
- Recover caustic solution
- Reduce downstream corrosion
- Eliminate potential reaction of caustic with MTBE blending.

Full-scale operation. Mol-RT installed a L/L coalescer system that contained 17 high-efficiency coalescer cartridges that were 40 in. in length and four in. in diameter. A pre-filter was also installed to remove solid particulates upstream of the coalescer. The sizing of the full-scale system was based on the pilot-scale L/L coalescer tests and was at an equivalent flux to 14 lpm through the test coalescer. This was well below the maximum test flowrate of 23 lpm and facilitated possible variations in the caustic water properties that may affect coalescing. The fluoropolymeric L/L coalescer cartridges were specially designed to remove caustic carryover from hydrocarbon streams.

The coalescer unit was started up in November 1995. After several months of operation, the following results were observed:

- Approximately 2,000 ppmv of caustic solution recovered by test coalescer (2 liter caustic/m³ gasoline)
- No haze in effluent. Gasoline was "bright and clear." Samples were cooled to 5°C with no haze observed.

The service life of the pre-filters was 6 months before requiring change-out and the L/L coalescers operated for 18 months. In this service, the service life for the pre-filter and coalescers exceeded the initial design requirements, and therefore, represented a low overall operation expense.

Phenol removal. Another advantage detected in the test was the removal of phenol. During tests, phenol concentration in the FCC gasoline was approximately 330 ppm in the coalescer influent. Because the phenol is concentrated in the aqueous phase, the coalescer was able to reduce the gasoline phenol content. The effluent phenol concentration was 270 ppm, representing an 18% reduction in phenol content in the gasoline. The phenol content in the coalesced water was 14,500 ppm.

From an economic standpoint, the benefits received by the caustic recovery justify the installation of the coalescer, with payback in less than one year. Other large benefits are anticipated due to the haze reduction in the gasoline and lowered downstream corrosion. Over the four years of operation, the average annual savings for caustic has been estimated at 126,000 lb/yr on a dry basis. New developments in coalescing technology have made it possible to separate very stable emulsions and dispersions by mechanical means. ■

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