

Emulsification
A solution to Asphaltene Handling Problems

Dr. Sundaram Logaraj^a, Tom Ernzen^a, Dr. Moon-Sun Lin^a, Todd Hays^a, Calvin Stegemoeller^a, Dr.
Li Feng^a, Tony Ng^a, Mark Stroder^a
^aAkzo Nobel Asphalt Applications

Dr. Stephen J. DeCanio^b, Ron J. McKeon^b, Shylaja M. Shirodkar^b
^bTexaco Inc.

Presented at the:

ISSA/AEMA 2nd Joint Conference
March 12-13, 2000
Amelia Island, Florida USA

Emulsification – A solution to Asphaltene Handling Problems

Dr. Sundaram Logaraj^a, Tom Ernzen^a, Dr. Moon-Sun Lin^a, Todd Hays^a, Calvin Stegemoeller^a, Dr. Li Feng^a, Tony Ng^a, Mark Stroder^a

^aAkzo Nobel Asphalt Applications

Dr. Stephen J. Decanio^b, Ron J. McKeon^b, Shylaja M. Shirodkar^b

^bTexaco Inc.

Abstract

The asphaltenes obtained from the deasphalting process are difficult to handle and pump because of their high viscosities and softening points (Ring & ball), which range from 80 to 300 °C. The asphaltenes have a fuel value better than that of coal and petroleum coke and are in general comparable in cost to that of coal. An economical process for converting asphaltenes to an easy to handle material by emulsifying with water is a desired option. Emulsification of asphaltenes and similar hard hydrocarbons with a softening point ranging from 80 C to 120 C will be discussed. Emulsification at a mix temperature as high as 165 C is possible. The dispersions of asphaltenes and other hard hydrocarbons in water produced by this process are more stable than normal paving grade asphalt emulsions. There are some limitations concerning the types of surfactants that can be used at these higher than normal emulsification or mix temperatures.

Emulsification – A solution to Asphaltene Handling Problems

Dr. Sundaram Logaraj^a, Tom Ernzen^a, Dr. Moon-Sun Lin^a, Todd Hays^a, Calvin Stegemoeller^a, Dr. Li Feng^a, Tony Ng^a, Mark Stroder^a

^aAkzo Nobel Asphalt Applications

Dr. Stephen J. Decanio^b, Ron J. McKeon^b, Shylaja M. Shirodkar^b

^bTexaco Inc.

Introduction

Asphaltenes

Asphaltenes are the bottom products from the solvent deasphalting of vacuum residuals, atmospheric residuals or other similar asphaltic material. Solvent deasphalting processes such as the ROSE process, upgrade these material by separating the heavy asphaltene fraction from the lighter fraction using a variety of solvents such as propane, iso-butane and n-butane. The softening point of the resulting asphaltene depends on the type of solvent used and could range from about 70 °C to about 300 °C. The asphaltnes have a fuel value around 17000 BTU/LB, which is better than coal and petroleum coke. In general the cost is comparable to that of coal.

Need for emulsification of asphaltenes

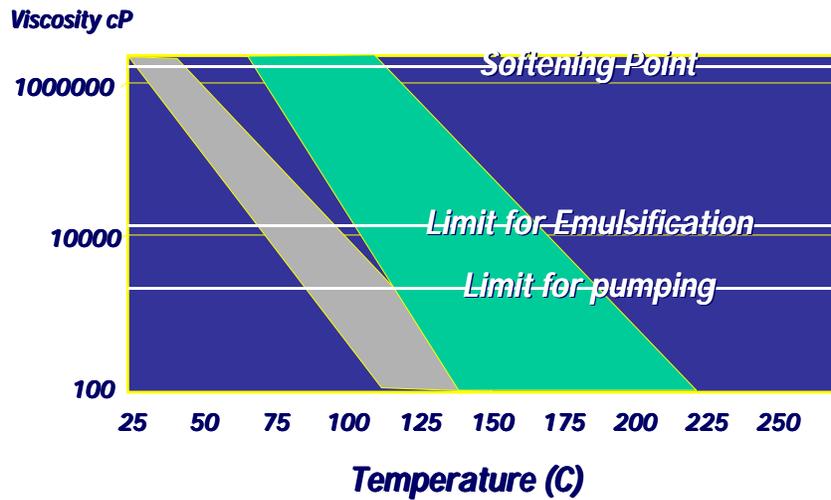
Asphaltenes are difficult to handle and pump because of their high viscosity and high softening point. Adding solvent to lower viscosity is uneconomical and there are practical problems in keeping the asphaltenes hot over extended periods of time. Emulsifying with water and a surfactant seems to be a potential alternative. Texaco was considering the ROSE process for their refineries, and had the idea to use asphaltene by-products as a fuel for a nearby power plant. Texaco was interested in emulsifying propane and butane extracted asphaltenes with a softening point ranging from 80°C to 120 °C.

Akzo Nobel and Texaco reached an agreement where Akzo Nobel would focus on developing the technology to prepare stable asphaltene dispersions in water and Texaco would focus on the end use which is the successful burning of the asphaltene dispersion as a fuel. In addition to the softening point Texaco specified that the dispersions should have a minimum asphaltene content of 65% and the cost of the surfactants used should not exceed \$7.00/Ton of asphaltene dispersions. The most important criteria is that the dispersions should be stable enough to be stored, transported, and pumped.

High temperature emulsification

A survey of earlier work showed that there was a limit on the softening point above which stable dispersions were until now not possible. This limit on softening point seems to be not above 70 °C or 80 °C. Normal asphalt with a softening point around 50 °C is emulsified at an emulsification or a mix temperature around 85 °C to 95 °C. At this temperature asphalt has a viscosity roughly below 20,000 cps.

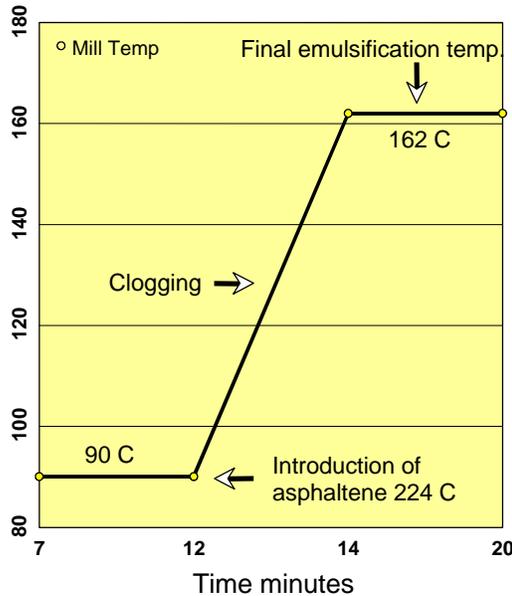
Figure 1
Viscosity of Asphalts and Asphaltenes



If an asphaltene with a softening point around 100 °C needs to be emulsified, according to Figure 1, the emulsification or the mix temperature should be around 150 °C. Theoretical calculations show that the most important parameter for emulsification is the emulsification temperature or the mix temperature. The time it takes for the asphaltene and surfactant solution (soap) to reach equilibrium temperature is extremely fast compared to the residence time in the mill.

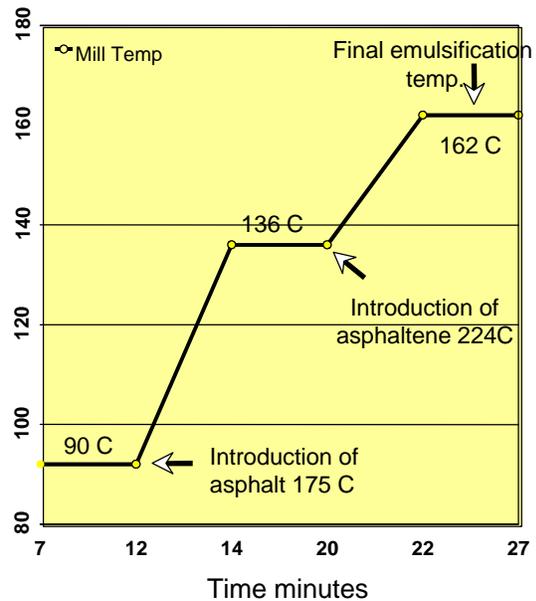
Figure 2

A. Emulsification start up
Earlier unsuccessful process



Asphaltenes R&B : >80C

B. Emulsification start up
with normal asphalt



Asphaltenes R&B : >80C
Asphalt (AC-20)

Earlier attempts to emulsify asphaltenes were unsuccessful because, although soap phase and asphaltenes were introduced to the colloidal mill at temperatures calculated to give the correct mix (emulsification) temperature, the mass of the colloidal mill takes some time to heat up to the desired final temperature. During this time asphaltenes are for some time at the temperature of the surfactant solution which is around 90 °C. At these temperatures asphaltenes are very viscose and almost a solid which makes them impossible to emulsify. Even if some emulsification takes place there is no pressure at the beginning of the process to prevent boiling of water. So water boils and the solid asphaltenes clogs the system (Figure 2). A separate issue addressed below is that not all surfactants are effective towards emulsification and in providing stability to the dispersions at these higher than normal emulsification temperature. In the modified processes shown in Figure 2B these problems are avoided by a special stepwise start-up of emulsification which uses regular asphalt or other material to bring the mill to temperatures and pressures before introducing asphaltenes.

Emulsification process

Calculation of Temperatures

A viscosity profile is run on the asphaltenes and the temperature above which the viscosity is below 20,000 cps is chosen as the emulsification or the mix temperature. The temperature at which the viscosity is about 1000 CP is chosen as the temperature of the asphaltenes for pumping purposes. Then based on the asphaltene content in the final dispersion one can calculate the temperature of the surfactant solution. To avoid the need to pressurize the soap lines, the soap phase temperature was limited to 90 –95 °C, effectively limiting the asphaltene softening point to about 130 °C. The required pressure that would prevent water boiling off is determined from steam tables.

Equipment

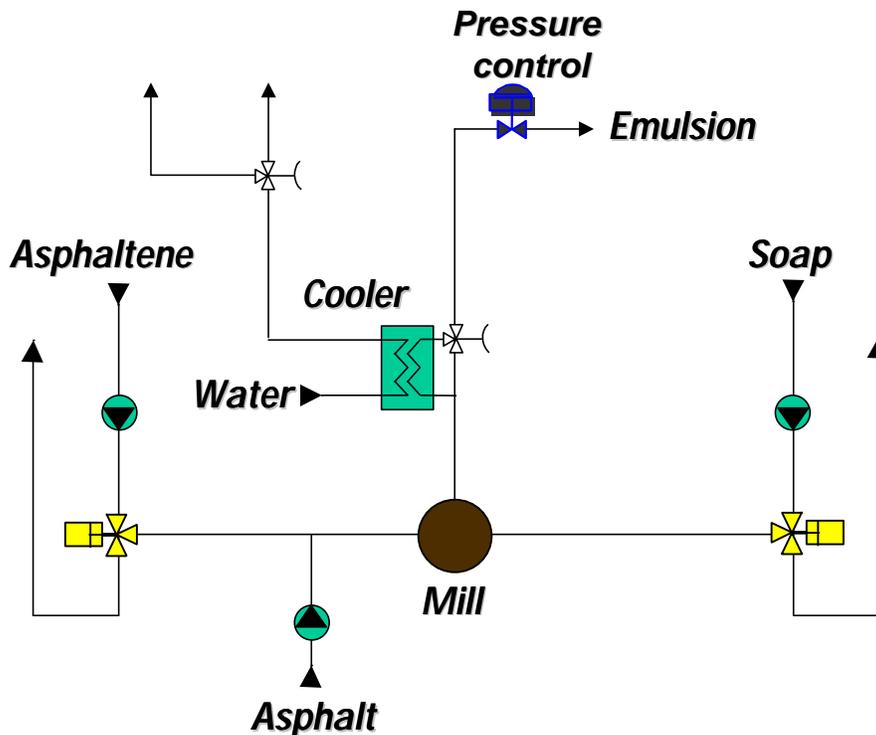
The schematic diagram of the apparatus used to emulsify the asphaltenes is shown in Figure 3.

Asphaltene with a softening point above 80 °C was used. First surfactant solution at a temperature of above 90 °C is fed into the mill followed by normal asphalt (AC-20) heated to a temperature around 175 °C instead of asphaltenes. Since asphalt has low viscosity at the temperature of the surfactant solution (90 °C) emulsification is started and soon the temperature of the mill raises to a mix temperature of around 136 °C. Also flow of the emulsion through the system and through the restriction in the pressure control valve creates a pressure. The valve was adjusted previously to give the desired pressure. At this stage asphalt is replaced by asphaltenes. Now asphaltenes has enough low viscosity at 136 °C that starts to emulsify and soon the temperature raises to the final mix temperature of 162 °C. Emulsification continues and the dispersions are cooled by the heat exchanger to below the boiling point of water before the pressure is released at the pressure control valve.

With this process it was possible to produce good dispersion but the process had some limitations in a laboratory scale plant. Since the flows are small, about 1 gallon/min the pressure control valve openings were very small. It takes some time for the mill to reach the final emulsification temperature after asphaltenes are fed into the mill. Any unemulsified material produced at this time slowly makes its way to the pressure control valve and clogs the system. Also accurate flow

controls were found to be essential since too little asphaltene flow would result in a not high enough emulsification temperature and too high an asphaltene flow would cause the emulsion to invert into a viscose, water in oil emulsion and clog the system. In addition, too high an asphaltene flow would result in a mix temperature at which the pressure established is not enough to prevent water boiling off.

Figure 3
Continuous production start up with Asphalt (AC-20)



Modified process with pressure tanks

In a modified system, the pressure control valves were eliminated and two pressure tanks were added which are shown in Figure 4. There is a line by passing the heat exchanger and going into the first pressure tank. The system beyond the mill is pressurized to the required pressure using a compressor. First surfactant solution is fed into the mill and through the heat exchanger into the first waste pressure tank. Then asphalt is fed into the system and the by pass line is opened to send the resulting emulsion into the waste tank. Then asphaltenes are fed into the mill replacing asphalt and as soon as the final emulsification temperature is reached the resulting dispersion is fed through the cooler and then into to one of the pressure pots.

Figure 4
Continuous production using pressure tanks

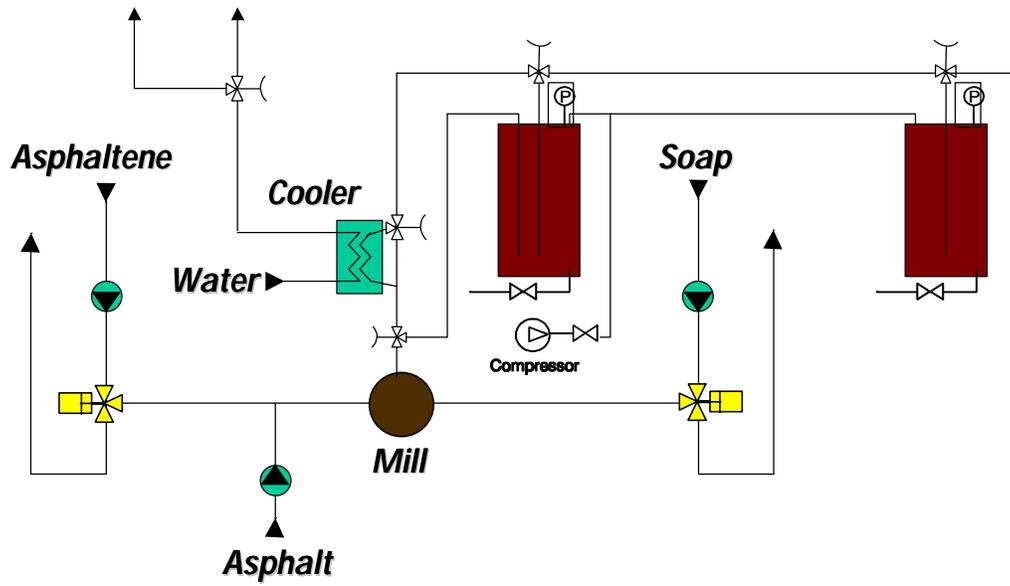
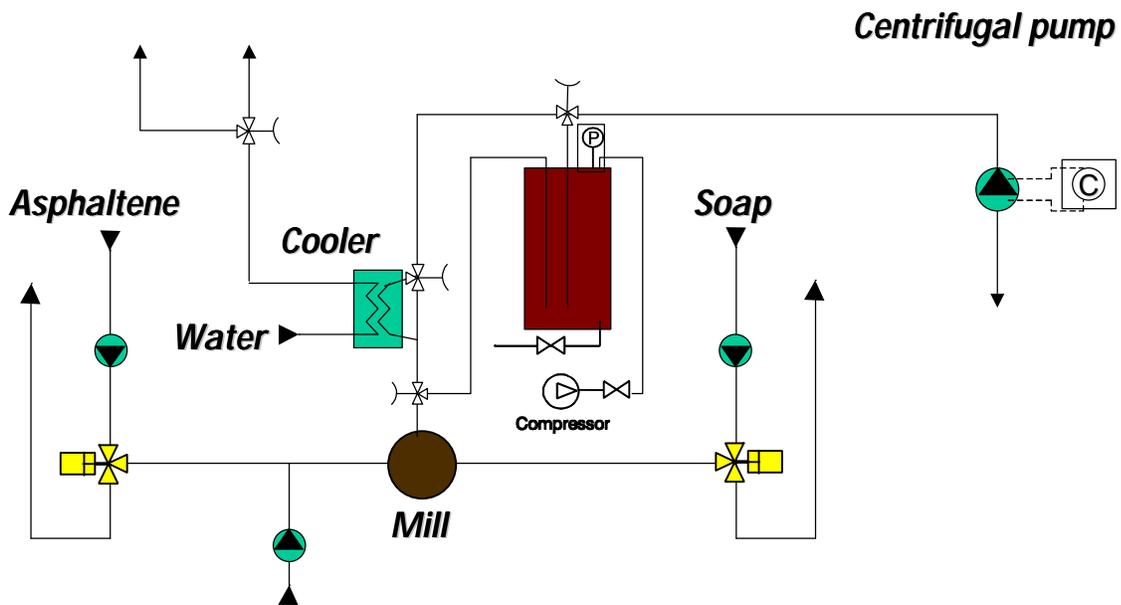


Figure 5.
Continuous production using centrifugal pump as a pressure control device



In a full-scale emulsion plant since the flows would be higher, the pressure control valves can have bigger openings and the use of pressure tanks would not be necessary. It was of interest to see if in the lab scale production, continuous production without producing into pressure tanks would be possible. In a modified lab scale plant a centrifugal pump running in a direction opposing the flow of the emulsion (Figure 5) was used to control the pressure. The pressure was possible to be controlled just by adjusting the RPM of the centrifugal pump. One pressure tank was used for collecting the start up production material which may have some bigger particles that would cause clogging of the heat exchangers and other restrictions. This pressure tank also may not be necessary in a full scale production where the flow of asphalt can be gradually decreased where at the same time the flow of asphaltene would be gradually increased to reach a 100% asphaltene flow.

Testing of dispersions, results and discussion

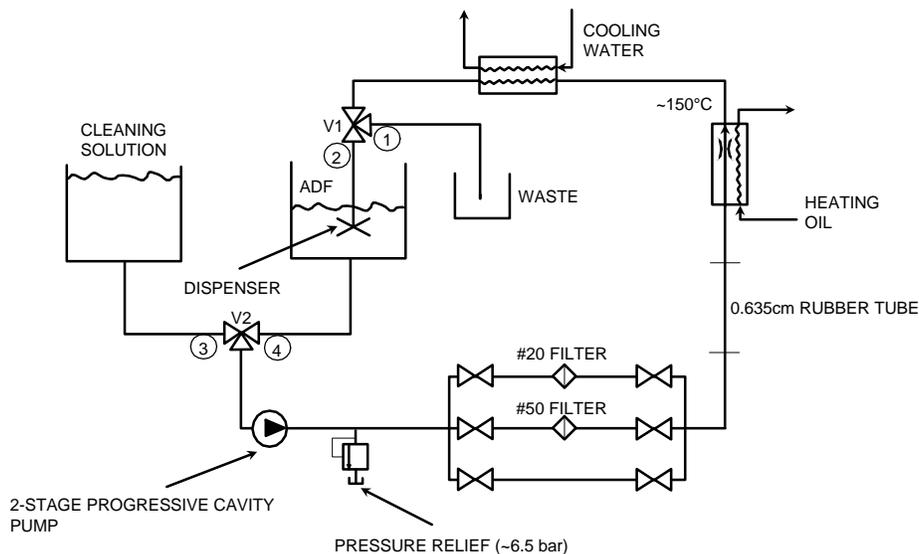
Several asphaltene dispersion samples were produced according to the modified procedure described above using the emulsification units represented by the flow diagrams in Figure 4 and Figure 5. A few tests were designed to evaluate the dispersions with respect to their storage, transportation, and pumping stability. The standard emulsion tests (ASTM D244) such as the “residue by evaporation” and the “24 hour storage stability test” were run on the dispersions.

Shaker test

A shaker test was designed to simulate the conditions of transporting in a tank truck. About 100 g of dispersion was shaken in a Burnell Wrist Action Shaker for 24 hours and then the dispersions are filtered through a #50 mesh screen. The amount of broken dispersion on the screen and in the bottle gives a measure of its stability towards transportation. A dispersion, which gives a residue below 1% of the weight of the dispersion, is considered to pass the shaker test.

Pump Test

Figure 6. Pump test apparatus



The dispersions were pumped using a Roper[®] 2-stage progressive cavity pump, running at a speed of 300 rpm. About 4 Kg of dispersion is first filtered through a 50-mesh screen and then placed in one of the two reservoirs. The dispersion was pumped at a flow rate of 8 l/min at a pressure of 5 bar from one reservoir to the other. The dispersions were pumped through a #50 mesh filter and a 0.635cm x 6m-rubber tube for creating steady pressure. The dispersions were circulated for about 20 minutes, which was equivalent to turning over the material about 58 times. The dispersion that can be pumped this way for 20 minutes and collects less than 10-g residue in the filter was considered to pass the pump test.

Particle size distribution

The particle size distribution was run using a Coulter LS 230 instrument.

Table. 1 lists some of the manufacturing conditions and the results of testing the various dispersions. The dispersions listed in the table pass the shaker and the pump tests. The particle size distribution of the dispersions was found to have a median well below that of normal asphalt emulsions. The particle size distribution also had a direct correlation with the various other properties of the emulsion. If the median is below about 4 microns and there is no significant amount of particles above 40 microns the dispersions seemed to pass the various stability and the pump tests. Along with progressive cavity pumps, diaphragm pumps and centrifugal pumps were also found to be suitable for pumping asphaltene dispersions. The results also indicated that the dispersions are more stable than normal asphalt emulsion. Coalescence is the main pathway by which emulsions deteriorate. The asphaltene droplets, when cooled become hard spheres and do not deform which is a necessity for them to coalesce.

Table 1. Properties of Asphaltene Dispersions

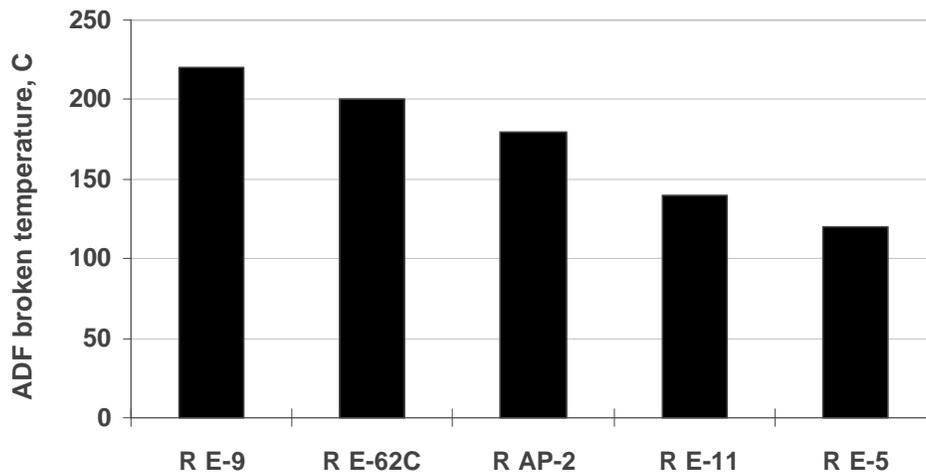
	Exxon	Cenex	Cenex
Softening point C (R&B)	118	104	104
Surfactant	0.5% Redicote E-9	0.5% Redicote E-9	0.5% Redicote AP2
pH of soap	2.1	2.2	11.7
Emulsification Temp. C	162	160	152
Shaker Test	Pass	Pass	Pass
Pump Test	Pass	Pass	Pass
Particle size (median microns)	1.7	2.6	2.3

Role of surfactants at higher than normal emulsification temperatures

During production there is a short period during which the dispersions are at high temperatures. This is in the mill and the space before the heat exchanger where the dispersions are cooled well below the boiling point of water. The surfactant gets its property by the stabilizing forces provided by the interaction of the hydrophilic group with water. The charged end group and the counter ion are solvated by water. These interactions are stronger in ionic surfactants compared to non-ionic surfactants. These interactions are weakened as the temperature increases and in the case of non-ionic surfactants where the interactions are based on hydrogen bonding becomes almost non-existent at these high temperatures. This would indicate that the non-ionic surfactants would be ineffective at these high temperatures and that was found to be the case. Even among ionic surfactants there was a difference between the various surfactants with different types of hydrophilic groups. Some surfactants were found to undergo thermal degradation at these high temperatures.

The high temperature stabilities were tested by sealing the dispersions in a steel tube and heating the dispersions to various temperatures using an oil bath. The tubes are then cooled in water and are opened. The dispersions were analyzed for particle size distribution to see if they have deteriorated.

Figure 7. High temperature limits for asphaltene dispersions made with various surfactants

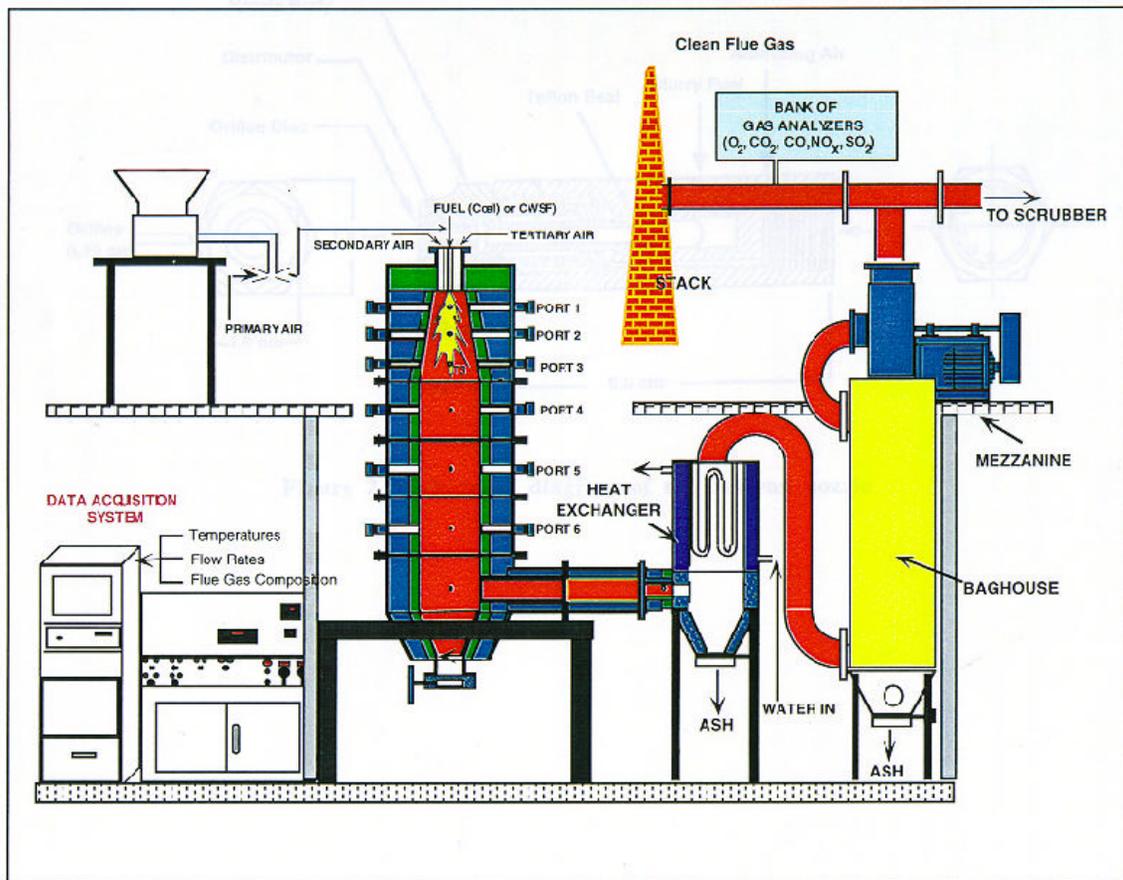


R = Redicote®

Drum Scale production and burn tests

Two pilot productions each of about 2 tons were successfully completed. Cationic surfactants were used and the asphaltene content in the dispersions were kept above 68%. The dispersions were shipped by land and air to Pennsylvania and to United Kingdom respectively. The dispersions were found not to deteriorate during this transportation process. The combustion behavior of the asphaltene dispersions was evaluated in the multi-fuel down-fired combustor (Figure 8). Gas samples can be extracted from any number of sampling ports located along the combustor or downstream of the combustor to continuously monitor the various exhaust gases. One of the main observations of interest was if it would be possible to continuously feed the asphaltene dispersions into the combustion chamber without clogging and if it would result in a self-sustaining continuous flame. The burn test showed that this was possible with the asphaltene dispersions. Some of the key factors for a successful burn test were the kind of pumps used and the design of the atomization nozzles. It is also necessary to keep the dispersions below the boiling point of water until it exits through the nozzle into the combustion chamber.

Figure 8. Down fired combustor



Summary and conclusions

Our experiments showed that emulsification at temperatures as high as 165 °C is possible. The same process was used to produce stable dispersions from Gilsonite blends with a softening point of 121 °C and polymer modified asphalt with more than 5% SBS polymers. The dispersions produced with asphaltenes and other hard hydrocarbons were found to be more stable than normal asphalt emulsions. They are storage stable, transportation stable, and could be pumped and burnt as a fuel using suitable pumps and burner designs. There was a difference in the behavior of surfactants at these higher than normal emulsification temperatures. The non-ionic surfactants were found to be unsuitable and even among the ionic surfactants some were better than others.

References

1. For previous work on emulsification at high temperatures and pressures see “Patents US 4,943,390; US 4,832,747; US 4,821,757; EP 07 32 376 A2; US 5,478,365”.
2. Chemistry of Asphaltenes, J. W. Bunger, N. C. Li, Advances in Chemistry Series 195, American Chemical Society, 1979.
3. Surfactants and Interfacial Phenomena, M. J. Rosen, A Wiley-Interscience Publication, 1978.