# Comparison of Rheological Properties for Recovered Residue from Emulsified Asphalt obtained by Three Recovery Procedures

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## Abstract

Subject area: Quality/Test Procedures

Several recovery procedures for asphalt emulsion residue have been used over the years, but there is no one procedure that has been universally accepted. In this study three recovery methods are used to obtain the residue of the emulsified asphalt:

1) distillation (ASTM D 6997),
2) evaporation (ASTM D 6934) and,
3) the newly approved moisture analyzer balance procedure described in ASTM D 7404.

Five types of emulsified asphalt used for different applications for various pavement treatments were investigated:

1) a cationic slow-set tack coat, diluted CSS-1h;
2) a cationic rapid set used for chip seals, CRS-2;
3) a solvent containing cationic medium-set CMS-2h;
4) ananionic high float medium-set, HFMS-2; and
5) a rapid-set polymer modified used for chip seals, CRS-2P.

The residue obtained from each emulsified asphalt was characterized by a Dynamic Shear Rheometer (DSR) by performing frequency sweep and a temperature sweep on each recovered residue. The preliminary rheological characterization of the binders performed at $60^0$C and $25^0$C show that the Complex Modulus, G* can be used to rank the recovery procedure for each emulsion type. Increasing G* was observed for all emulsion types: G*(D-7404) > G*(D-6934) > G*(D-6997) except for CRS-2P where the G* was comparable for all three recovery procedures. These preliminary rheological results suggest that aging of the binder during recovery for the three methods is ranked as moisture analyzer balance (D 7404) > Evaporation (D-6934) > Distillation (D 6997). Master curves were generated for each emulsion residue using the temperature and frequency sweep. Furthermore the extrapolated crossover frequencies deduced from the master curves for the residues obtained by the different recovery methods are shown to be a way to assess the 'cured' state of the residue and to differentiate the procedures.

## 1. Introduction

The residue of emulsified asphalts is used as a key specification and quality control parameter for manufacturers and state agencies alike. It is important for monitoring emulsified asphalt production, since it is an indicator of asphalt content and indirectly of viscosity. This allows for an optimization of formulation for any given emulsion. For this reason the emulsified asphalt residue needs to be generated in a timely and precise fashion. However, current standard methods for residue recovery of emulsified asphalts continue to be time consuming. Currently in the United States there are over ten different recovery methods [1, 2] and three that have been accepted as consensus standards and are outlined in ASTM and AASHTO standards [3-5]. A recent TRB publication reviewed recovery procedures for both USA and the European Union [2] and a new residue recovery procedure using a moisture analyzer balance (MAB) has been published by ASTM [5]. A forced-air drying procedure to recover residue was compared with recovery from a rotating thin film oven test (RTFOT). The final residue was characterized by DSR [7]. Recently, a new recovery procedure based on a low temperature evaporative protocol has been proposed at ASTM [8]. This procedure takes 48 hours to obtain a residue. A European evaporative method similar to ASTM is also used [9].

The new MAB procedure along with the other accepted methods are the subject of this study. One of the issues with the consensus procedures is that polymer modified emulsions have not been addressed adequately. It is interesting to note that in the original Superpave standard performance specifications the use of polymers in hot asphalt was not addressed in a very consistent rheological manner and is just now been address. However in the case of polymer modified emulsions the issue is; what temperature is best to use for the recovery of binder that has been polymer modified. The new recovery method that has been proposed uses a lower temperature to recover the polymer modified asphalt; however the procedure has not been tested extensively to whether or not it has addressed the problem of conserving the integrity of the polymer modified binder that will reflect the true performance characteristics of the binder in the field.
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The premise is that any laboratory procedure to recover the residue from any emulsified asphalt, unmodified or modified, should not exceed the application temperature in the field. This is not the case for the distillation ($T > 200^{o}C$) and the evaporation procedures ($T = 163^{o}C$) that are widely used where recovery procedures exceed application and end-use temperatures. The goals of this research are two:

1) compare the MAB procedure with the consensus recovery standards that are now used, namely, distillation and evaporation, and

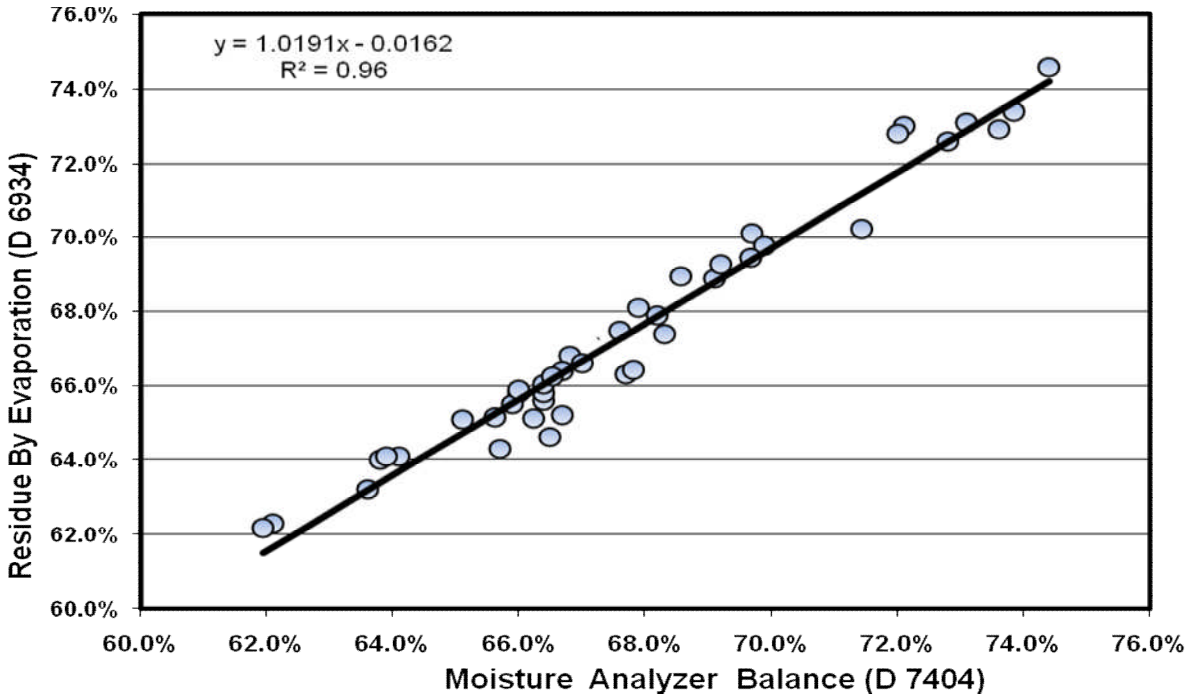
2) perform preliminary rheological characterization of the recovered residues from all three procedures.

The rheological characterization is in place of the traditional tests for penetration, ring and ball, and ductility. The emulsion industry as a whole is beginning to search for ways to apply rheological tests that relate to performance applying similar rheological concepts to the recovered binders from the emulsions that have been successful in Superpave binder characterization.

It is assumed that the recovered binder continues to be a viscoelastic material and therefore a similar rheological characterization of the binders may be applied. The difference is that the final rheological testing for these ‘surface’ treatment binders will be determined by application temperatures in the field. These temperatures are invariably below $100^{o}C$. The key to the rheological properties is that the binder is subjected to temperatures that are similar to application temperatures of asphalt emulsions in the field. This study is not to define end-use performance, but to show characterization of the residue obtained from the three procedures that were studied.

Figure 1 shows a good correlation between emulsified emulsion residues recovered by evaporation and the MAB procedure. This study now includes the distillation recovery procedure and some preliminary rheological data to further make a more solid comparison between these emulsified asphalt recovery procedures.

**Figure 1. Comparison Residue by Evaporation (D 6934) vs. Moisture Analyzer Balance (D 7404)**




## 2. Experimental Design

### *2. 1 Materials*

The determination of emulsified asphalt residue was performed on five different emulsified asphalts using three different recovery methods as described. The five emulsions represent a cross section of emulsions used for various pavement treatments: CSS-1h dilute, a slow set cationic use for tack coat or fog seal; CRS-2 rapid set unmodified cationic used for chip seal applications; CRS-2P polymer modified cationic rapid set use for chip seal; HFMS-2 a solvent containing anionic high float medium set use for cold mix application, including recycling; CMS-2h a solvent containing cationic medium set use for cold mix application. The base asphalt used for all emulsions was a PG 52-28, except that a PG 64-22 was used for the CSS-1h and CMS-2h.

### *2. 2 Equipment*

A Carrimed CSL 100 dynamic shear Rheometer equipped with a parallel plate was used to perform all rheological tests. The distillation equipment was a standard still as described in ASTM D 6997. For the Evaporation procedure ASTM D 6934 was followed. The moisture analyzer balance was a Sartorius model MA30 equipped with metal tubular design heater element. In all cases a nominal 5 g sample of the emulsion was used to recover the residue. The procedure followed here was ASTM D 7404.

### *2. 3 Test Protocol and Residue Recovery*

Emulsified asphalt samples were prepared according to the procedure described in each of the ASTM procedures. Variation of ASTM D-7404 [5] was as follows: the residue from the solvent containing emulsions, CMS-2h (with diesel solvent) and HFMS-2 (with kerosene solvent) were recovered at 162 $^0$C. The residue for the other emulsions, CSS-1H, CRS-2, and CRS-2P were obtained at 110 $^0$C. The analyzer was programmed such that it stopped automatically when the change in weight was within 1 mg for more than 140 seconds. In all cases, sample size was typically 5 grams of emulsion. After drying, the sample was transferred to the DSR for measurements. The residue recovery was complete within 20 minutes, compared to the evaporation procedure (3 hrs) and the distillation (2 hrs).

### 2.4 Complex Modulus Master Curves

Temperature sweeps were performed at 10$^o$C, 15$^o$C, 25$^o$C, 35$^o$C, 45$^o$C, and 60$^o$C and frequency sweeps done at 0.1 to 10 Hz. The master curve was then obtained using the time-superposition principle and using 25$^o$C as the reference temperature.

### 3.0 Results and Discussion

Table I shows values of the complex shear modulus, G* obtained from measurements with the dynamic shear Rheometer. The binder residue was obtained from five different emulsions types and recovered by the three different ASTM procedures.

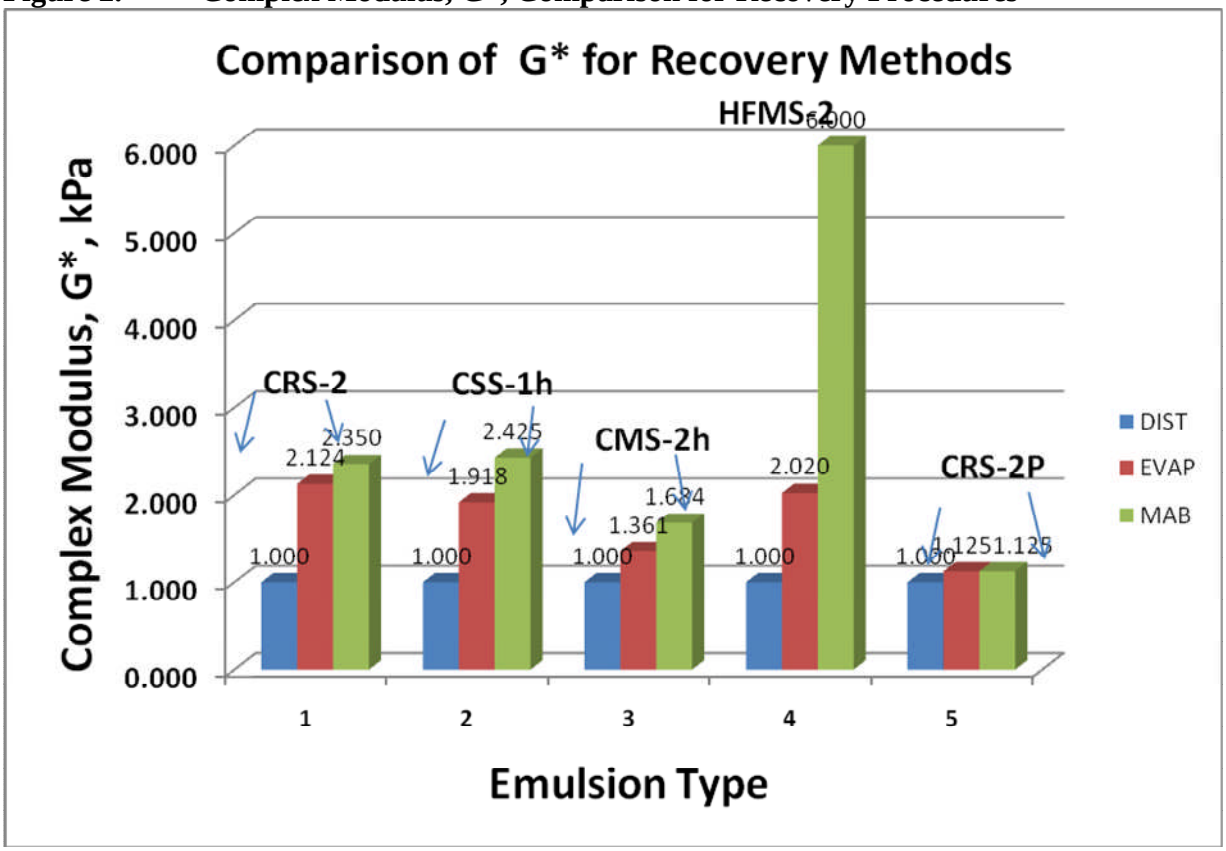
**Table I. Complex Modulus, G* for Residue Recovery Procedures**

| | G*( kPa )@ 60 C, 0.4 Hz | | |
|---|---|---|---|
| **Emulsion Types/Procedure** | Distillation, ASTM D 6997 | Evaporation, ASTM D 6934 | Moisture Analyzer, ASTM D 7404 |
| CRS-2 | 0.234 | 0.497 | 0.550 |
| CSS-1h | 0.730 | 1.400 | 1.770 |
| CMS-2h | 0.772 | 1.051 | 1.300 |
| HFMS-2 | 0.150 | 0.303 | 0.900 |
| CRS-2P | 0.800 | 0.900 | 0.900 |

The smallest differences in G* for the three procedures was observed for the polymer modified emulsified asphalt, CRS-2P. The largest difference in G* was observed for the high float anionic emulsion, HFMS-2.

The results are best summarized in graphical form and given in Figure 2, where values are obtained by normalizing the results from each procedure relative to the distillation procedure.

**Figure 2. Complex Modulus, G*, Comparison for Recovery Procedures**




The Complex shear modulus, G*, obtained at 60°C is used to compare how the rheological properties of the recovered binders changed for each emulsion type and for each procedure. In all cases, as seen in Figure 2 the distillation procedure had the lowest G*. Residues obtained from CMS-2h and CRS-2P, show G* values close to twice that of the residue obtained from the distillation. The G* for the recovered binder for CRS-2P appear the least affected by the three procedures. The G* for the binder recovered from the HFMS-2 emulsion is not easily explained, since it had the highest G* for all the emulsions for the moisture analyzer recovery procedure. The three procedures differ in the dynamics of their recovery. Whereas distillation and evaporation may be considered as more dynamic recovery procedures in the sense that samples are recovered under more turbulent conditions, boiling and stirring respectively compared to the static moisture analyzer procedure. Moreover, the surface-to-volume ratio for samples used in the MAB, considered a static recovery procedure, are much larger than samples used in the other procedures. Therefore, for the Moisture analyzer procedure the sample is more susceptible to oxidation than for the other procedures. However, this should diminish at lower recovery temperatures for the moisture analyzer and be investigated accordingly. Except for the G* of the recovered binder for the HFMS-2 emulsion, the evaporation and moisture analyzer recovery procedures are closer in their G* value despite the much longer recovery time (3 hrs) for the evaporation procedure

## 4. Master Curves Comparison for Recovered Binders

Master curves (figs 3-7) for the residues were obtained from the five emulsions and with the three procedures to compare their rheological properties. The reference temperature was 25°C. Except for the HFMS-2 emulsion the complex modulus was similar for the other residues. Comparison of the unmodified

emulsion CRS-2 with the polymer modified CRS-2P shows that the differences for the three methods for these two binders were minimal.

**Figure 3. CSS-1h Recovered Binder G* Master Curve**

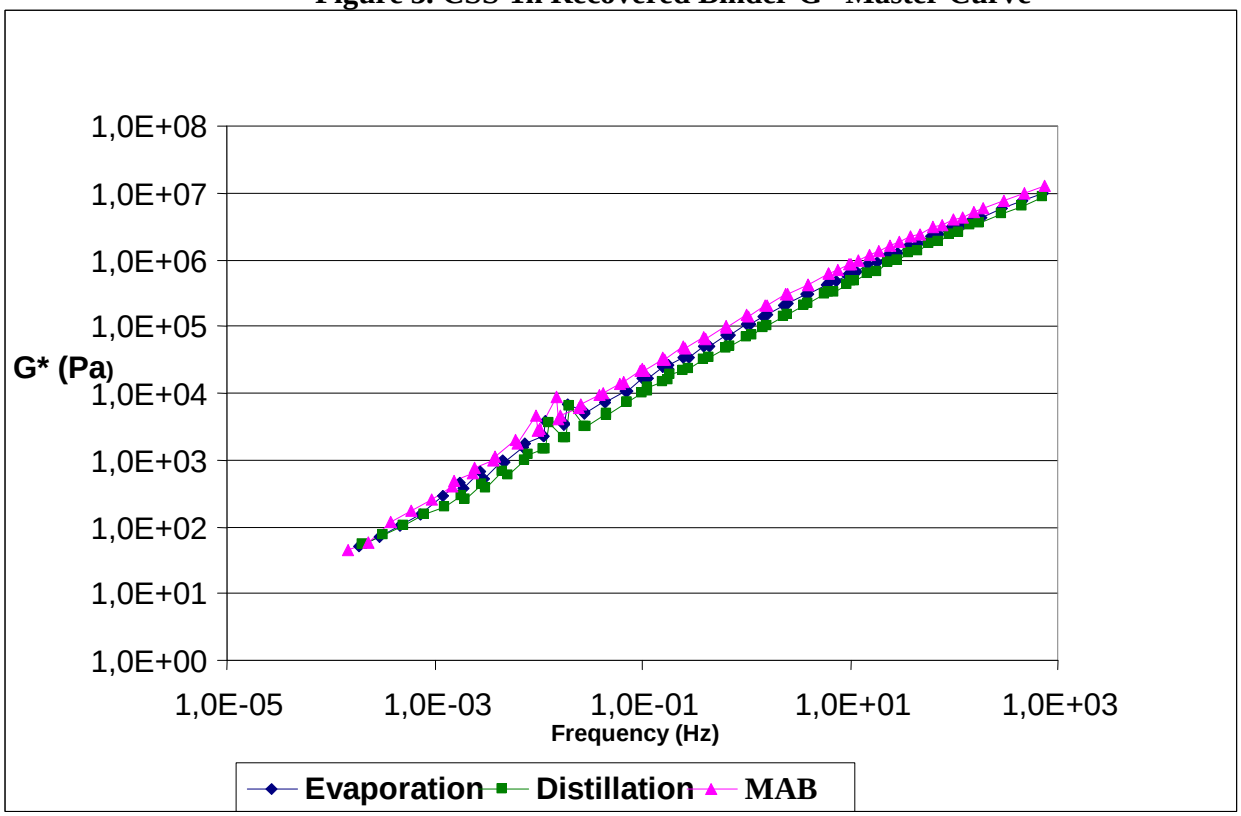



**Figure 4. CRS-2 Recovered binder G* master curve**

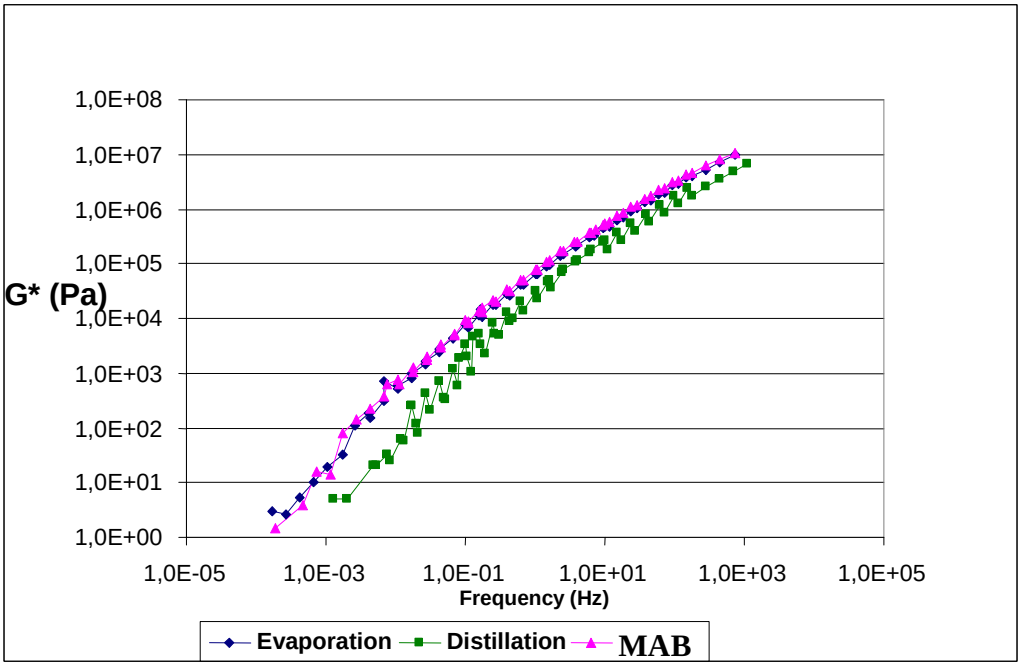


**Figure 5. CMS-2h Recovered binder G* master curve**

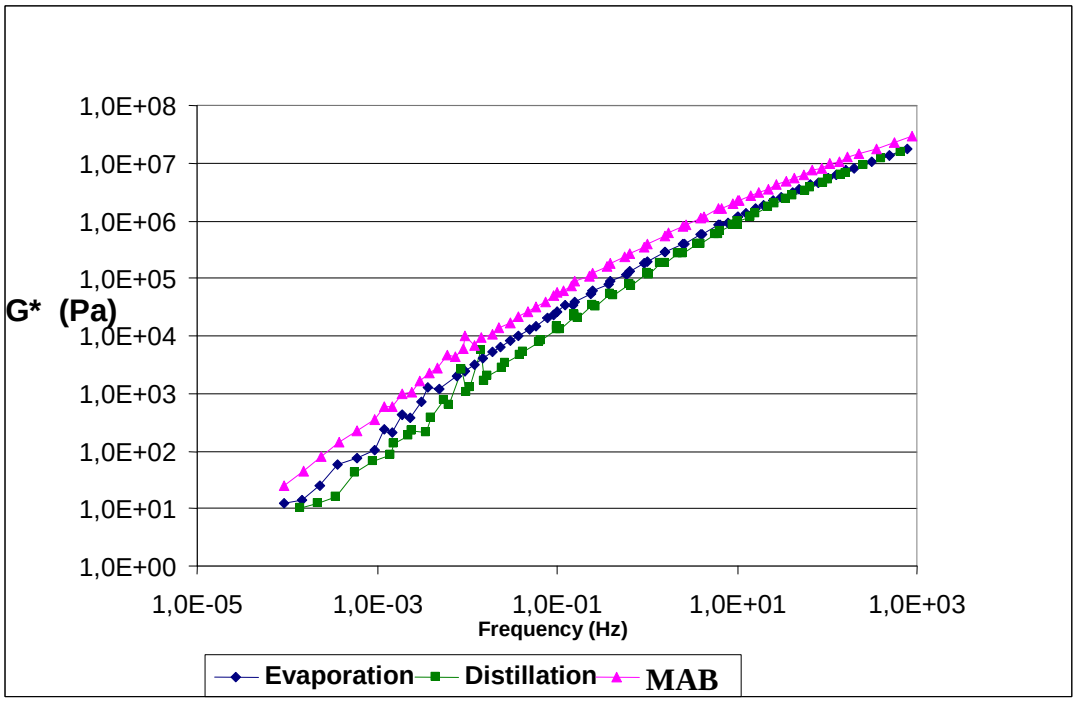



**Figure 6. CRS-2P Recovered binder G* master curve**

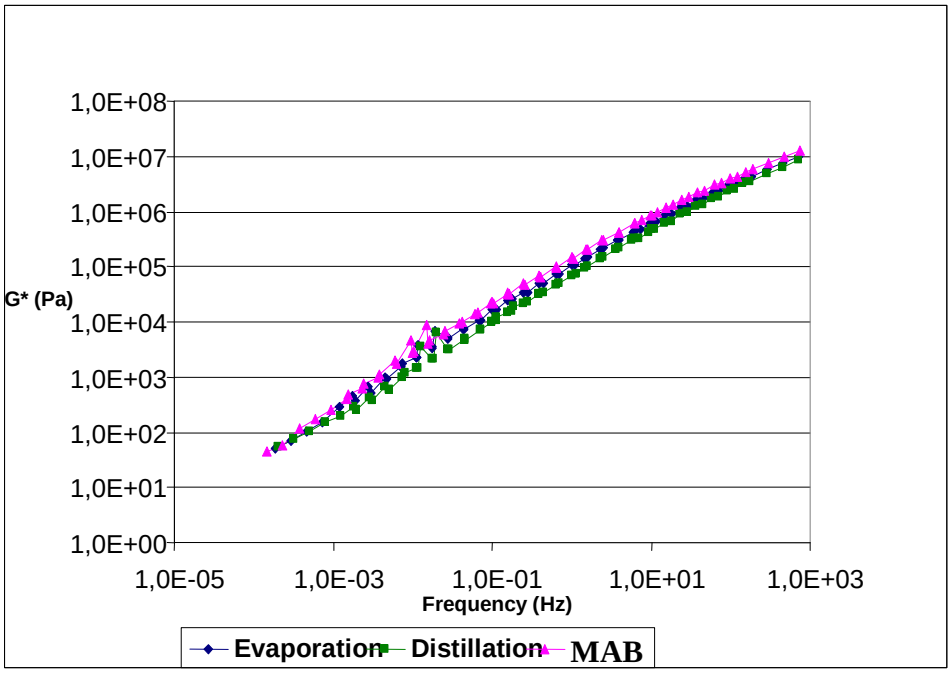


**Figure 7. HFMS-2 Recovered binder G* master curve**

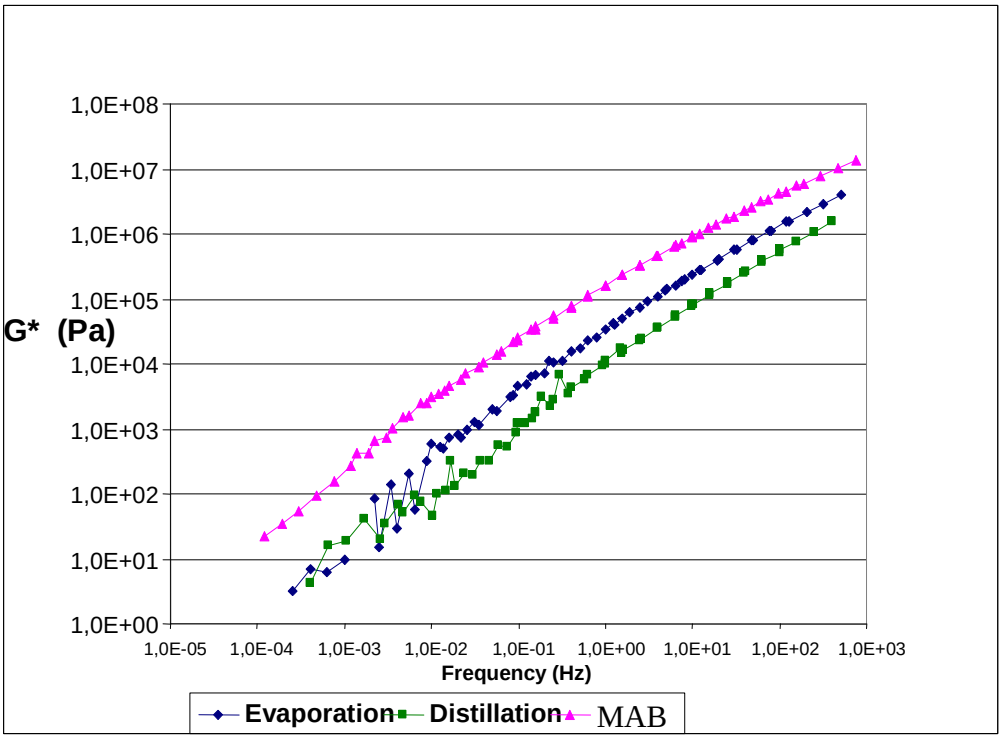
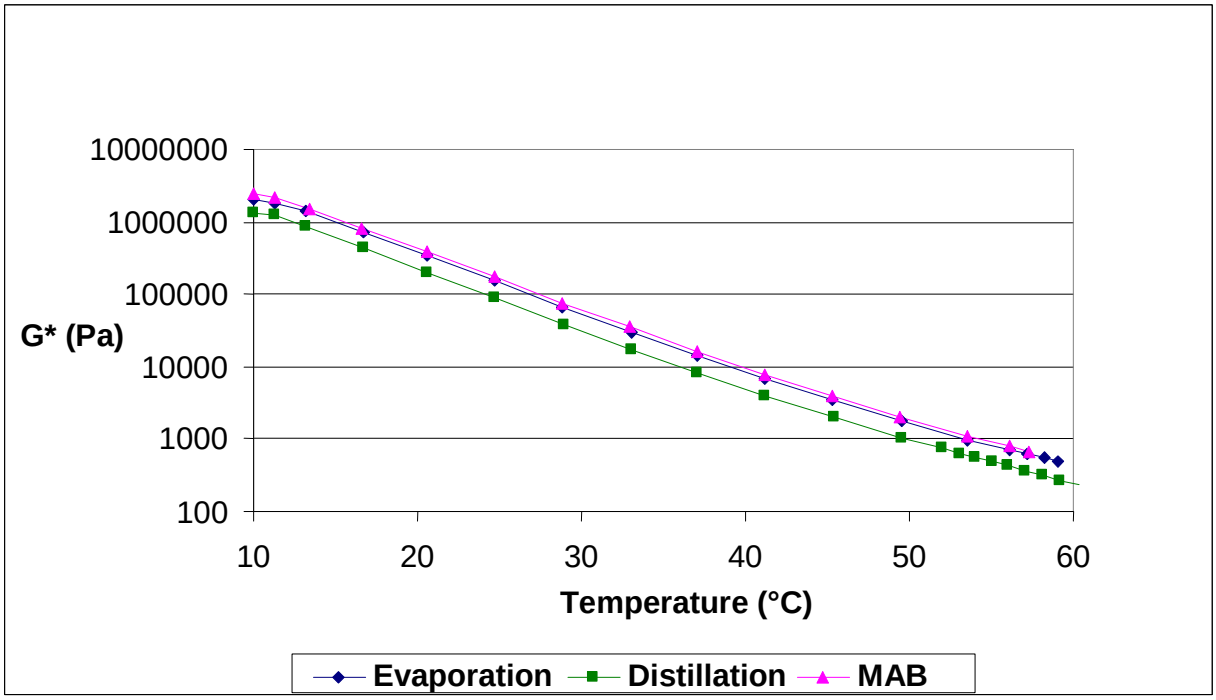
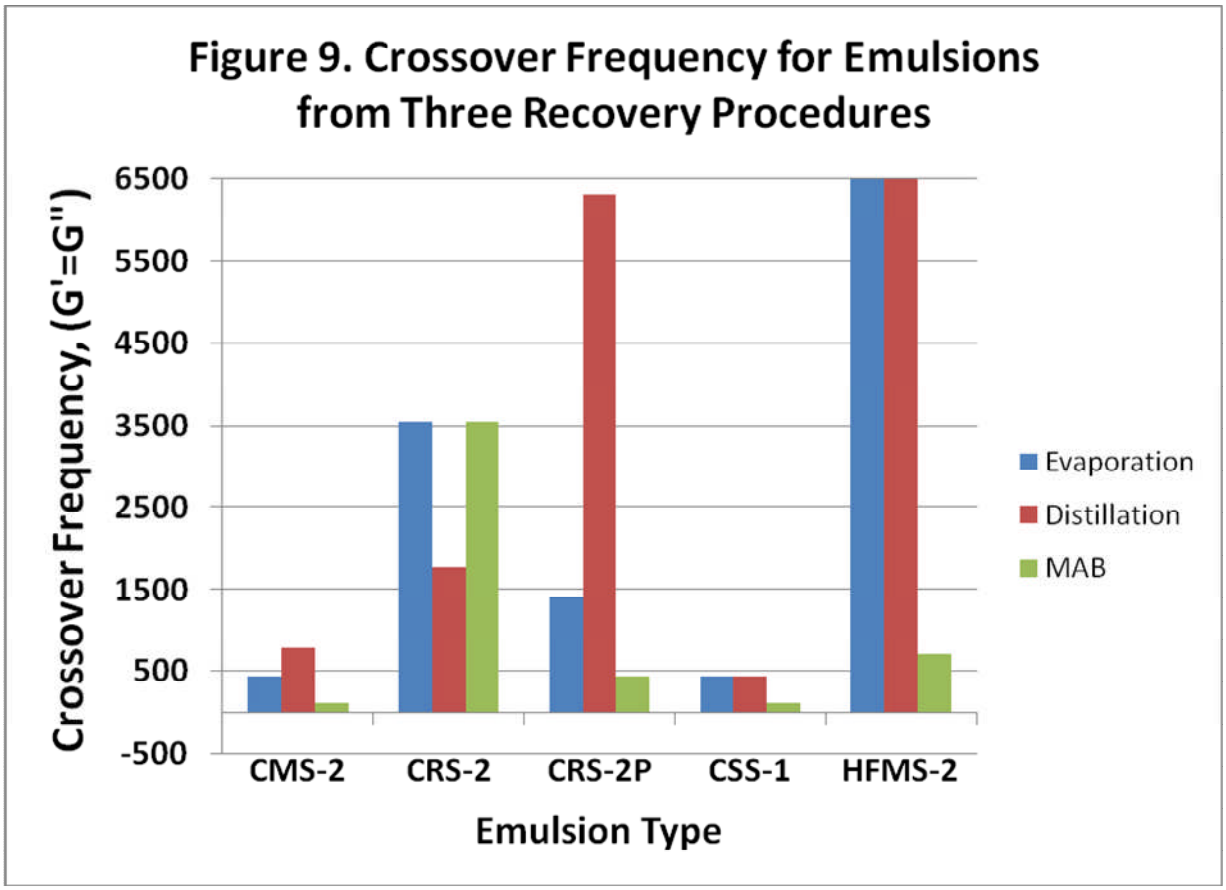



**Figure 8. G* for CRS-2 Temperature Sweep at 0.4 Hz for Recovery Methods**



In Figure 8 is shown the temperature sweep of the G* for CRS-2 for the three recovery methods. The sweep plots for the other four emulsions are similar. The important observation here is that the slope is the same for all three methods which is interpreted to mean that there is no significant rheological differences in the property of these binders regardless of the recovery method. As discussed previously the MAB has a larger G* than for the other recovery methods and this is likely due to the static recovery method with a larger surface-to-volume ratio of the sample which in turn leads to a higher oxidation. This is easily corrected by performing the recovery at a lower temperature and/or excluding air during the recovery.




It is interesting to compare the crossover frequency (G”=G’) for all five emulsions obtained from the frequency sweeps for the three recovery procedures. These are given in Figure 9 above and detailed in Table II below. These crossover frequencies are also referred to as the characteristic modulus, G [10]. When G’ > G’’ the residue behavior becomes more “cured” and more solid like, therefore the lower the characteristic frequency the “quicker the recovery procedure. This is the case for MAB procedure, except for CRS-2 where the distillation shows a more ‘cured” state than the other methods. This cannot be explained at this time. In general the evaporation and distillation recovery procedures show higher crossover frequency and in particular for the high-float anionic emulsion, HFMS which has is thought to be a more “gel” like emulsion. The lower characteristic modulus observed for CMS-2h and CSS-1h for all three methods is attributed to the “harder” binder used, PG 64-22, to make these emulsions and therefore attained a more solid-like behavior earlier than residues from the other emulsions made from a PG 52-28.

## 5. Conclusions

Three recovery methods were used on five different emulsions to obtain their respective residues and subsequently perform rheological tests on the binders. In general, it is observed that the recovery methods as performed in this study can be ranked based on the magnitude of the G*. The ranking of the recovery methods in terms of the G* is as follows: G*(MAB) > G*(Evaporative) > G* (Distillation). This intimates that there is a higher oxidation of the binder during recovery for the MAB method. This is due to the static nature of the recovery procedure and to the higher surface-to-volume ratio of the sample compared to the evaporative and distillation methods.

The MAB residue determination had a shorter test cycle time and used less material compared to the other two methods where testing times are at least five times as long and samples size is significantly larger. Further, the crossover frequency, or characteristic frequency, can be used to assess the "cured" state of the emulsion and can be used as a way to differentiate the recovery procedures.

Further work is in progress to reduce oxidation in the MAB recovery procedure and to recover the binder directly in the mold of the DSR rather than recover separately and then transport to a DSR for final testing. This will be reported in due course.

## Acknowledgements

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