PARAFFIN PROBLEMS IN LOW PARAFFIN CONTENT CRUDE

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ABSTRACT

Forty crude oils having 10% or less paraffin content were examined for their potential to deposit paraffin. The deposition was then correlated against several crude oil characteristics. It was found that the paraffin cloud point and the paraffin content were the two most important factors which dictated deposition potential. Viscosity versus temperature plots allow estimation of both paraffin cloud point and paraffin content. Pour point was not a factor in dictating deposition. It is suggested that a cloud point depression test is a better method than a pour point depression test for choosing a paraffin inhibitor. This is true only for low paraffin content crudes. However, there does not appear to be any quick test which allows one to predict the best paraffin inhibitor 100% of the time.

INTRODUCTION

Paraffin deposition in production tubing and surface flow lines has long been a problem. The deposition has caused problems ranging from plugging of surface lines to breaking of pump rods to plugging of formations during stimulation treatments. Paraffin has also been blamed for the difficulty of pumping crude oils at cool temperatures. A great deal of time and money has been spent removing this troublesome deposit. Such removal methods include paraffin dispersants, paraffin solvents, hot oiling, and mechanical scrapers.

Attempts have been made over the years to develop methods of preventing paraffin deposition. Such methods include the use of plastic coatings[1,2], surface wettability control[3], and wax crystal modifiers[4,5]. Testing methods for choosing a deposition inhibitor include cold spot tests[1,2], cold pipe tests[2,6], and pour point tests[7]. Recently, fluid rheology has been used to study the effect of crystal modifiers and other chemical additives on the flowability of crudes at cool temperatures[4,8,9]. Some workers have concluded that a chemical which gives a substantial reduction in the pour point of a crude is then a candidate to be a paraffin inhibitor for that crude[7]. One might also expect the same conclusion from flowability studies. Most of the crudes used in these studies have paraffin contents in the range of 10 to 40%. One might then expect that an oil with less than 10% paraffin content must not have paraffin problems. Unfortunately, this is not the case. There are many producers who have oil wells with low bottom hole temperatures producing crudes containing 0 to 10% paraffin. Some of these wells experience severe paraffin deposition problems. Furthermore, many of these problem crudes do not exhibit pour points above -20°F. This led us to study the deposition tendencies of low paraffin content crudes. Therefore, the intent of this work was to learn how to analyze a crude so that a statement could be made about the depositional tendency of that crude. It would also be desirable to find a quick screening test for choosing a paraffin deposition inhibitor.

THEORETICAL APPROACH

The oils used in this study were first characterized. This characterization included pour point, paraffin content, asphaltene content, paraffin chain length distribution, cloud point, viscosity versus temperature plot, and API gravity. Deposition tests were conducted at a constant cooling differential. The amount of wax deposited was then correlated against the various crude oil characteristics. Statistical analysis was used to analyze the correlations. This type of analysis provides the F statistic and a significance probability labeled PR > F. The PR > F answers the question, "What is the probability of randomness giving just as good of a correlation fit?". Thus, a PR > F of 0.10 says that there is only a 10% chance of randomness giving a larger F statistic. For this study, a PR > F of 20% or greater was considered to indicate no substantial relationship between the dependent and independent variables. A PR > F of 10% or less was considered to indicate a strong trend between the dependent and independent variables. Plots were made of all correlations giving a PR > F of 0.10 or less. These plots were then examined to determine if the correlation was real or if it was an artifact due to a single stray data point.

Several of the oil characteristics were redetermined after treating the oils with paraffin deposition inhibitors. These characteristics included pour points, cloud points, and viscosity versus temperature plots. Deposition tests were also conducted. The ability of the inhibitors to change the oil characteristics was compared to the deposition inhibition results. Inhibitor performances in the various tests were correlated with the original oil characteristics. The intent was to find a method to predict in which oils the inhibitors would work the best.

TEST METHODS

The oils were characterized using various test methods. Pour points were determined using ASTM D97-66. Asphaltene content was defined as that portion of the crude which was insoluble in petroleum ether. Paraffin content was determined using U.O.P. Method No. A-46-64. Paraffin chain length distribution was determined by gas chromatography of the isolated paraffin. API gravity was determined using ASTM D287-67.

Cloud points were determined using viscosity versus temperature plots.[10] Kinematic viscosity was measured using a Cannon-Fenske Viscometer size No. 150. The oil was warmed in the viscometer for 30 minutes using a water bath set at 120°F. The viscosity was then measured and recorded. The bath was cooled 10°F and the viscometer allowed 15 minutes to reach thermal equilibrium. The oil viscosity was then measured and recorded. This was continued until a temperature of 30°F had been reached. The same oil sample remained in the viscometer during the entire test. The data were then plotted on semi-log graph paper. Two straight line segments were drawn through the data points. The intersection of these lines gave the cloud point. Three additional pieces of information were used from these plots. One was the hot viscosity which was defined as the viscosity measured at 110°F. A second was the cold viscosity which was defined as the viscosity measured at 40°F. The third was the viscosity rise, or delta viscosity, which was defined as the viscosity difference between the hot and cold viscosities.

Deposition tests were conducted by stirring the oil at 80 to 90°F in front of a cold plate at 20 to 30°F. Deposition time was 7 hours. The amount of wax deposited was measured and recorded. Percent deposition inhibition by an inhibitor was defined as the percent of the original deposit that did not deposit when the test was rerun using an oil containing an inhibitor. Thus, if the original deposit was 1.0 g and the deposit with inhibitor was 0.2 g, then the percent deposition inhibition was 80%.

RESULTS AND DISCUSSION

Deposition Correlations

The results of correlating deposited wax in the deposition tests with the various crude characteristics are reported in Table 1. The results of cross correlating the various crude oil characteristics are reported in Table 2. The data in Table 1 show that the deposited wax showed some correlation with the cloud point, cold and delta viscosity, paraffin content and pour point. However, Table 2 shows that the cold and delta viscosity are directly related to the paraffin content. Thus, these two variables are not independent variables. A multiple correlation of deposited wax with the cloud point, pour point, and paraffin content gave a poor PR > F of 35%. The cause of the poor fit is due to the pour point. The reason is because there were several crudes that did not give pour points above -22°F but still gave paraffin deposition. A PR > F of 2.7% was obtained by a multiple correlation of deposited wax with the cloud point and paraffin content. This simply says that both variables strongly influenced the wax deposition. The regression parameters were used to plot the predicted wax deposits against the observed wax deposits in Figure 1. The data points would all fall on the line of slope = 1 if the model gave a perfect fit. This figure shows that the model accounts for most of the variation in the data. However, the model predicts higher deposition than actually observed at the low deposits.

There are several possible sources for the inadequacy of the model. First, the relationship between wax deposition and the independent variables may not be linear. That is, as the wax builds up on the cold plate the cooling rate slows down. This is due to the insulating effect of the wax. The net effect would be a reduction of deposition rate as the wax builds up. This effect would be more pronounced for the high wax depositing crudes. Second, the experimental error in the deposition tests is about 20%. Third, there may be another variable involved such as mixing which was not accurately taken into account in the testing program.

The model does allow some very interesting conclusions. First, the pour point of a low paraffin content crude oil cannot be used to predict paraffin deposition tendencies. Second, the chain length of the wax in solution does not appear to affect deposition tendencies. However, the chain length may have a profound effect on the texture of the deposited wax. This effect was beyond the scope of this work. Third, the two main controlling factors in deposition appear to be cloud point and paraffin content. This manifests itself in several ways. Production rates which get produced crude to the surface with temperatures well above the cloud point should show little deposition in the production string. However, high production rates of a gas phase can cause a substantial amount of cooling. This can cool the crude below its cloud point long before the crude has reached the surface and may result in severe deposition. The decrease in formation pressures over the life of a reservoir can cause increased production of the light ends and result in the loss of the wax solubilizing portion of the crude. This can result in the cloud point rising to a higher temperature. Thus, the deposition would occur sooner (lower) in the tubing.

Cross Correlations

Cross correlation results of the various crude oil characteristics are reported in Table 2. There are several interesting points uncovered by these results. For example, the cloud point of a crude appears to be independent of the paraffin content, asphaltene content, paraffin chain length, and pour point. This is in contrast to work done on high paraffin content oil in which the asphaltene content had a marked effect on the cloud point.[10] It is also interesting that the amount of wax in solution does not effect the temperature at which it comes out of solution. This stands in stark contrast with systems such as solutions of salt in water. It is not at all clear what determines the cloud point of a low paraffin content crude. However, the light end content of the crude could be responsible.

Another point of interest in Table 2 is the pour point. The pour point appeared to be independent of paraffin and asphaltene contents, cloud point, and API gravity. It had a slight correlation with the cold (40°F) viscosity. However, this can be discounted when one realizes that many oils had substantial cold viscosities even though they did not exhibit a pour point above -22°F.

Another useful piece of information is apparent from the cross correlations. That is, the delta viscosity, or viscosity rise upon cooling, is directly related to the paraffin content in the crude. The PR > F was 1.0% for this correlation. It is fortunate that this correlation exists because one can now obtain a qualitative estimate of deposition tendency from a viscosity versus temperature plot. Such a plot allows one to determine the cloud point and relative paraffin content in the crude. From this information, one can predict whether paraffin will be a problem even before substantial production has begun. It is suggested that keeping a record of these plots for a given well or field can be informative. For example, if a non-paraffin problem well shows a substantial rise in cloud point, then it can alert the operator that paraffin deposition may soon occur. The operator can then be prepared with a paraffin maintenance program. This would certainly be preferable to finding out about a paraffin problem after costly mechanical problems have occurred.

Finally, it was found that the hot (110°F) viscosity correlated well with the API gravity. This was of little value since an oil's density can be determined by simpler methods.

Deposition Inhibition

Paraffin deposition inhibition tests were conducted when sufficient quantities of oil were available. The results of these tests are summarized in Table 3. These data show that Inhibitor A was the preferred paraffin deposition inhibitor. This inhibitor showed activity in all but 4 (13%) of the tested crudes. This compares with a 40% failure rate for the other two inhibitors. Inhibitor A showed greater than 80% inhibition on 39% of the tested crudes. This compares with only 12% for Inhibitor B and 0% for Inhibitor C. All three inhibitors are proprietary nonionic copolymers of varying molecular weight.

It would be desirable to understand in which type of crudes the various inhibitors gave the best performance. For example, does Inhibitor A work best in the higher paraffin content crudes? Does Inhibitor B work best in low gravity crudes? To answer these questions, the deposition results for each inhibitor were correlated with API gravity, cloud point, cold viscosity, paraffin chain length, paraffin content, and pour point. None of the correlations gave satisfactory results. Therefore, one must conclude that an accurate inhibitor recommendation cannot be made on the basis of crude oil characteristics alone. That is, an inhibitor test of some kind must be performed on the oil.

Depression Tests

The effect of the three inhibitors on cloud point depression, cold viscosity depression and pour point depression was examined. This was accomplished by measuring the cloud point, cold viscosity, and pour point of the crudes containing 0.1% of an inhibitor. The depression results were used to predict which inhibitor would perform the best in the deposition inhibition tests. The best inhibitor predicted would be the one which depressed the variable of interest the most. As such, pour point depression predicted the correct inhibitor 15% of the time, cold viscosity depression predicted the correct inhibitor 21% of the time, and cloud point depression predicted correctly 32% of the time. When cold viscosity and cloud point depressions were used together, then the correct inhibitor was predicted 42% of the time. In this latter method, the best cloud point depressant was chosen. If the cloud point was not depressed, then the best cold viscosity depressant was chosen.

One can conclude that the cloud point method of predicting inhibition was more accurate than the pour point method. However, one could have achieved a 72% success rate by simply guessing that Inhibitor A was the best in every case. It was noticed that if Inhibitor A gave greater than a 2°F cloud point depression, then the inhibitor was effective at deposition inhibition. Also for Inhibitor A, if the cloud point was not depressed but the cold (40°F) viscosity was depressed by at least 10 centistokes, then the inhibitor was still effective at deposition. The other two inhibitors did not show this trend. There were several cases with all three inhibitors in which the inhibitors showed good activity on the inhibition tests but poor activity on the depression tests. Therefore, the only accurate way to choose the best deposition inhibitor is by running a deposition test. This can be done by either running deposition tests in a laboratory or by running field trials.

CONCLUSIONS

(1) The tendency for paraffin deposition from low paraffin content crude is governed by paraffin content and cloud point.

(2) Viscosity versus temperature plots give information concerning paraffin content and cloud point.

(3) Cloud point depression tests have some utility in deposition inhibitor testing methods.

(4) Pour point depression tests are of little value for choosing a deposition inhibitor in low paraffin content crudes.

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Table 1
Correlation of Wax Deposition with Crude Oil Characteristics

Oil Characteristics	Number of Points	PR > F*
API Gravity	21	0.4193
Asphaltene Content	15	0.3314
Average Chain Length	22	0.5569
Cloud Point	21	0.0916
Cold Viscosity	19	0.0591
Delta Viscosity	19	0.0755
Paraffin Content	26	0.0383
Pour Point	10	0.1140
Cloud Point and Pour Point and Paraffin Content	11	0.3519
Cloud Point and Paraffin Content	22	0.0274

Table 2
Cross Correlation of Crude Oil Characteristics

Dependent Variable	Independent Variable	Number of Points	PR > F*
Cloud Point	Paraffin Content	27	0.8621
Cloud Point	Asphaltene Content	19	0.1431
Cloud Point	Average Chain Length	25	0.2249
Cloud Point	Pour Point	13	0.6855
Pour Point	Paraffin Content	19	0.8377
Pour Point	Asphaltene Content	8	0.9562
Pour Point	API Gravity	13	0.3217
Cold Viscosity	Pour Point	11	0.1104
Delta Viscosity	Pour Point	11	0.1144
Cold Viscosity	Paraffin Content	25	0.0203
Delta Viscosity	Paraffin Content	25	0.0103
Hot Viscosity	API Gravity	27	0.0001

*The PR > F statistic answers the question, "What is the probability of randomness giving just as good of a correlation fit?" Thus, the smaller the PR > F, the stronger the correlation.

Table 3
Deposition Inhibition Results

Number of Additives	Oils Tested	Percentage of Oils Giving Inhibition > 80%	> 50%	< 20%
Inhibitor A	31	39%	74%	13%
Inhibitor B	26	12%	42%	42%
Inhibitor C	21	0%	43%	38%

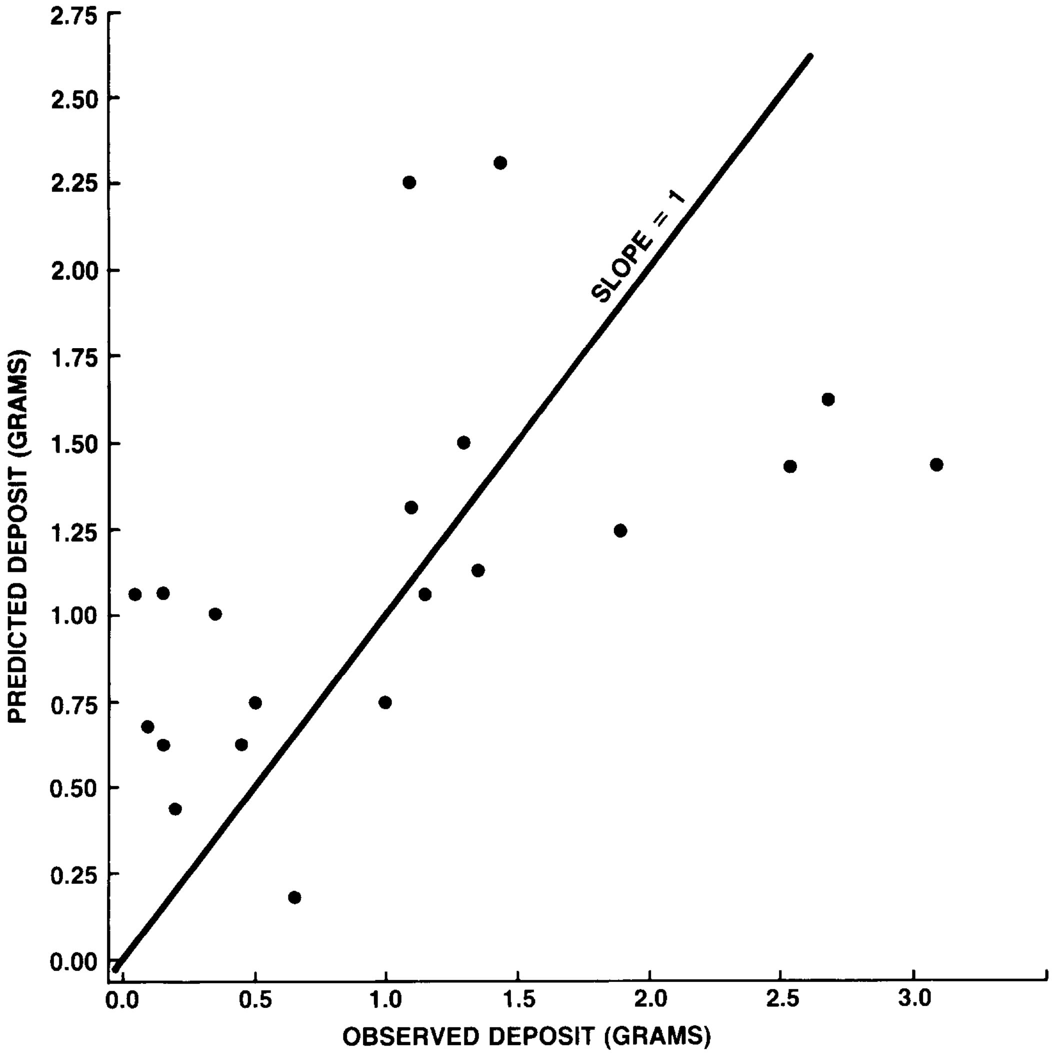

Figure 1 - Comparison of regression results with observed results