

**WHAT ARE SOLUBLE MACROMOLECULAR
OXIDATIVELY REACTIVE SPECIES (SMORS)?**

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INTRODUCTION

The search for diesel fuel components which can be linked to insolubles or sludge formation as a product of oxidative aging has led to some interesting new findings recently. Pre-filtered fuel which is oxidatively aged under accelerated conditions which simulate one to two years of ambient storage is filtered to determine the product insolubles formed. If the filtrate is then subjected to size exclusion chromatography (SEC), no intermediate molecular weight or size components are observed. If the fuel-insoluble product which has been removed by filtration is solubilized and subjected to identical SEC analysis, a broad peak centered on 600 to 800 daltons is the principle chromatographic feature. If the aged fuel is not filtered and simply dissolved in SEC mobile phase, numerous species of varying molecular size can be detected in the range of 150-1000 daltons. The higher molecular weight features of these chromatograms are very similar to the fuel-insoluble product after aging; the lower molecular weight features are what one would expect if oxidation and condensation reactions of fuel monomeric species were consecutively reacting to form the ultimate fuel-insoluble high molecular weight product. However, the absence of these intermediate molecular weight species in the filtered fuel leads to the unconventional conclusion that oxidation of fuel monomeric species is not responsible for sludge formation.

A second related finding is that after extraction of unstable diesel fuels and light cycle oils (LCOs) with methanol, the tendency of these stocks to form insoluble sediment upon oxidative aging is greatly reduced (1). This finding is illustrated in Table I, where four blends of 30% LCO in straight run from four separate refineries are subjected to aging in the low pressure reactor at 90° C for 24 hours at 100 psig oxygen. The pass/fail criterion is about 6 mg/100 ml. The samples were extracted with strong aqueous base and with methanol (described in experimental section below). The methanol extracted fuels are greatly stabilized in all cases regardless of the relative stabilities of the unextracted control samples.

Table II illustrates the effect of methanol extraction on either the straight run distillate or LCO portion used to make up the blend. It is readily apparent that the insolubles precursors are primarily associated with the LCO portion. More remarkable is the fact that the isolated methanol extract can be dissolved in a hydrocarbon solvent (which by itself does not form insolubles under the LPR aging conditions) and after aging an insoluble sediment can

be isolated. In two of the three blends (B-3 and B-4) a remarkable mass balance is achieved in that the sediment from the extracted blend plus the sediment from the methanol extract in solvent equals the sediment in the unextracted blend. For B-5 the methanol extract in the solvent formed even more sediment than the original fuel blend. These results indicate clearly that the precursors to fuel-insoluble sediment are very efficiently extracted into the methanol.

Attempts were made to analyze the methanol extract from a range of unstable LCOs in order to determine the gas chromatographable monomeric fuel components responsible for insoluble sediment formation. It was not possible to correlate any particular compound or compound class present in the relatively easily analyzed methanol extract as being responsible for the product insoluble sediment.

Evaporating the methanol extracts to dryness led to an intractable tar. Attempts to weigh the tar were abandoned due to the impossibility of achieving constant weights. If this tar is carefully precipitated with hexane, it is possible to isolate a dark solid material which is filterable on a 1.2 micron glass fiber filter. This solid material may be washed with hexane, dried and weighed. The material has been named soluble macromolecular oxidatively reactive species (SMORS) (2). Typical values for SMORS from a variety of straight runs and LCOs are given in Tables III and IV. Again it is apparent that the reactive LCO generally contains SMORS at varying levels, as determined by a simple methanol extraction and hexane precipitation. This led to the observation illustrated in Figure 1 that the weight of SMORS in any catalytically cracked LCO was linearly related to that LCOs tendency to form fuel-insoluble sludge after oxidative aging.

This paper presents additional information about the physical and chemical nature of the SMORS and the nature of their role in blends with straight run distillate streams. The possible use of the simple SMORS determination as a substitute for traditional accelerated storage stability tests in certain cases will also be discussed.

EXPERIMENTAL

All of the fuels and blend stocks fell within ASTM D975 diesel fuel number 2 specification requirements. Most of the much more stringent U.S. Navy Distillate Diesel Fuel specifications (MIL F 16884) were also met by almost all of the fuels and blend stocks. The fuel code used throughout the tables is: SR = straight run distillate, LCO = catalytically cracked light cycle oil, B = a blend of SR + LCO, a number following any of the letter codes refers to a different refinery source. Fuel sources were primarily US in origin but several European samples are included.

The storage stability test utilized is described in detail elsewhere (3) and utilized the so-called low pressure reactor (LPR) at 90° C and 100 psig oxygen for various periods of time.

All fuel samples are first pre-filtered using Gelman Type A/E glass fiber filters before either extraction or aging. The methanol extraction procedure uses fuel/methanol volumes of 100 ml/40 ml in a 250 ml separatory funnel. The two phases are vigorously shaken for about 90 seconds and the system allowed to settle until good separation occurs, typically 2-5 minutes. The fuel layer is then drawn off and discarded and the methanol phase is decanted into a 125 ml brown borosilicate bottle which is immersed to the neck in a boiling water bath to evaporate the methanol. In order to achieve good repeatable quantitation, it is absolutely essential that all the methanol is driven off because of the very high solubility of the hexane insoluble fraction of interest in methanol. After evaporation the sample is allowed to cool to room temperature. About 50 ml of filtered ACS reagent grade hexanes are then added to the bottle and any hexane insoluble material is precipitated. The sample is then vacuum filtered through a pre-weighed 47 mm Gelman type A/E glass fiber filter in a Buchner funnel, rinsed well with hexane and allowed to dry thoroughly before weighing again. If constant weights are not achieved with ambient air drying the samples may be oven dried at about 60° C for an hour. When it is desirable to recover the solid material from the filter for subsequent analysis a 0.8 micron Millipore type AA or a Nylon 66 filter may be substituted for the glass fiber filter, and a Millipore filtering apparatus for the funnel.

RESULTS AND DISCUSSION

The SMORS can be quantitatively isolated either before or after an accelerated aging test (on a separate aliquot if before the aging test). It is important to note that the SMORS solids should not be confused with the product insoluble sediment solids. The product insoluble sediment is removed from the post aged fuel by filtration and then the post aged filtered fuel may be extracted to determine the SMORS solids after aging.

Size exclusion chromatograms of representative samples of the SMORS solids both before and after stress tests were obtained. The chief characteristic was a molecular weight peak of about 700 to 900 daltons. Qualitatively and quantitatively the chromatograms of the SMORS were similar for all LCOs both before and after aging. In addition, the physical appearance and solubility characteristics of the SMORS was similar for all of the LCOs.

The nature of the SMORS led to their descriptive acronym. They are soluble in diesel fuels. They are macromolecular, that is, they are much greater average molecular weight than the diesel fuel range. They are oxidatively reactive species, that is, they are apparently primarily responsible for the oxidative formation of sludge products in the fuel.

The SMORS are not just precursors to sludge formation in catalytically cracked LCOs but are apparently prerequisites in a necessary but not sufficient regard. The examination of SMORS in many diesel fuels has led us to propose the values in Table V as a possible compositional requirement governing storage stability. If a fuel contains a high (>30 mg/100 ml) concentration of SMORS, problem levels of sludge formation are inevitable at ambient conditions in less than 6 months. If the concentration of SMORS is very low (<1 mg/100 ml), irregardless of fuel source, composition and refining process no fuel related sludge formation will take place even after very long storage at ambient. At intermediate levels (1 to 30 mg/100 ml) it would be advisable to further scrutinize the fuel by running a realistic accelerated stability test.

The physical appearance and nature of SMORS is very intriguing. The fact that they are particulate and filterable on a 0.8 to 1.2 micron filter indicate that they are physically similar to the product insoluble sediment. It has been suggested by Chertkov, et al (4) that the product solid phase is not formed by the oxidation of fuel components but is present in the fuel in the form of a colloidal system. Oxidation of the fuel leads to the destruction of this colloidal system and precipitation of the solid phase. They believe that this higher molecular weight material already existent in the fuel is responsible for sludge formation in both diesel and jet fuel. Further they claim that this material should be similar to petroleum asphaltenes except in their much higher oxygen incorporation.

In an effort to extend our understanding of the chemical nature of the SMORS, we investigated the effect of several straight run streams on several LCOs. A high acid (SR-5A) and a low acid (SR-11) fuel was blended into various LCOs and the SMORS yields determined before and after a 24 hour LPR test. The product insoluble sediment was also determined. Table VI illustrates two representative LCOs. The effect of the straight runs regardless of their acid content is not simply that of diluent to the SMORS. For either LCO we would calculate about 14 mg on the basis of dilution for the 40% v/v case and 7 mg for the 20% v/v LCO case. In both cases (pre-stressed) we obtain about double the calculated weight of SMORS. As usual, with either LCO the straight run blends give higher amounts of insolubles than the starting LCO itself. It is quite interesting that the low acid SR yields almost double the high acid SR blend for either LCO. Yet the effect on SMORS is invariant regardless of acid level before or after aging.

Since the addition of the straight run seems to favor the partition of SMORS into the initial methanol extract, we next investigated the effect of a pure hydrocarbon model for the SR on the effect of SMORS yields. Hexadecane was chosen as the diluent and the effect on LCO-5 is given in Table VII. The effect of the pure hydrocarbon diluent is to drive the partition coefficient even more into the initial methanol extract. It is interesting to note that even when the dilute blends are aged about twice the insoluble

sediment is formed over the neat LCO case. The pre-stressed SMORS expressed on a 100 ml LCO basis are 30 to 50% increased in the dilution range of 20 to 80% v/v hexadecane.

This leads us to consider not so much the nature of the SR or diluent phase as controlling the various amounts of product insoluble sediment as the nature of our original determination of SMORS in the blends. In blends, it becomes of greatest importance to maximize the partition coefficient of the initial extraction into methanol. This, then, would allow us to determine if the SMORS (however isolated) are the primary controlling reagents in product insolubles formation.

Since the effect of strong acid addition to blends of catalytically cracked LCO in SR exerts such a pronounced effect on the insoluble sediment production of these fuels (5), we examined the effect of such acid addition on the yields of pre-aged SMORS. Table VIII illustrates our results for LCO-14 with and without the addition of 0.010 M chloroacetic acid. Remarkably the SMORS yields were increased about four fold. This concentration of this acid addition to LCO/SR blends generally has the effect of increasing the product sediment yields by about somewhat less than ten fold. Since Tables VI and VII show the effect of increasing the SMORS yields simply by adding an SR diluent, the effect of adding acids to SR/LCO blends would be predicted to increase the SMORS yields somewhat more than the four fold increase of added acids to the neat LCO. The effect of added acid to the LCO may indeed be nothing more than the destruction of an already existent colloidal dispersion in the cracked LCO material, leading to the production of greater amounts of insoluble sediment.

CONCLUSIONS

The original scheme for isolating this new class of material from fuel (the SMORS), has been extended in the current work. The effect of SR or pure hydrocarbon dilution of the LCO on SMORS yields reveals that the original levels determined in the neat LCOs themselves is probably on the low end. This leads to a desire to maximize the partition coefficient into the initial extractant phase. The addition of an organic acid at low concentration has been shown to have the desired effect and will be pursued using additional acids and blends of LCO/SR in addition to other LCOs.

SMORS are important pre-requisites and precursors of sludge formation in aged diesel fuels. This makes the further refinement of the physical isolation method of SMORS an important area of study. In addition, the further detailed characterization of the SMORS may aid fuel producers and users in minimizing the deleterious impact of this material by selectively controlling and realistically predicting its effects.

REFERENCES

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TABLE I. Results of KOH and Methanol Extraction on Insolubles Formation. Aging test is LPR at 90°C, 24 hours, 100 psig oxygen. Pass/Fail criterion is 6 mg/100 ml.

Fuel Blend	Mg insolubles/100 ml		
	Control	KOH Ext.	MeOH Ext.
B-2	1.4	2.0	0.8
B-3	9.4	9.2	2.2
B-4	6.8	3.8	2.4
B-5	11.4	10.6	2.0

TABLE II. Effect of Methanol Extraction on 3 Reactive Fuels. Aging as in Table I. Series 1 = unextracted 70/30 blends. Series 2 = 35 ml extracted SR blended with 15 ml LCO. Series 3 = extracted 70/30 blends (MeOH). Series 4 = 35 ml SR blended with 15 ml extracted LCO. Series 5 = MeOH fraction from series 3 suspended in 25/75 butylbenzene/dodecane.

Fuel Blend	Mg insolubles/100 ml		
	B-3	B-4	B-5
Series 1	10.2	8.2	12.6
Series 2	10.8	7.2	14.6
Series 3	4.0	3.2	2.2
Series 4	5.0	3.2	4.4
Series 5	6.6	5.0	19.6

TABLE III. Weight of Solids Isolated from the Hexane-insoluble Fraction of the Methanol Extract of 7 SR Fuel Stocks. Aging as in Table I.

Fuel Code	Hexane Insolubles (mg/100 ml)		Insol. Sed. (mg/100 ml)
	Pre-stress	Post-stress	
SR-3	0.0	ND	0.0
SR-4	0.1	0.1	0.0
SR-5A	0.7	2.0	0.6
SR-5B	0.0	0.6	0.4
SR-11	0.0	0.1	0.1
SR-12	0.2	ND	0.0
SR-13	0.1	0.1	0.3

TABLE IV. Weight of Solids Isolated from the Hexane-insoluble Fraction of the Methanol Extract of 8 Cracked LCOs and 1 Blended Diesel Fuel. Aging as in Table I.

Fuel Code	Hexane Insolubles (mg/100 ml)		Insol. Sed. (mg/100 ml)
	Pre-stress	Post-stress	
LCO-1	112	116	27.0
LCO-2	14	17	3.3
LCO-3	53	63	13.0
LCO-4	27	40	3.4
LCO-5	92	114	20.0
LCO-12	1	14	4.7
LCO-13	2	101	33.0
LCO-14	2	58	4.0
B-3	14	18	8.2

TABLE V. Use of SMORS (mg/100 ml) as Simple Compositional Test for Predicting Storage Stability of any Mid-distillate Fuel.

Weight of SMORS (mg/100 ml)	Insoluble Forming Tendency	Action
<1	Fuel has indefinite storage life	No accelerated stability test needed
<30 and >1	Fuel stability generally worse at higher SMORS levels	Accelerated stability test required
>30	Fuel will degrade significantly in less than 6 months	No accelerated stability test needed

TABLE VI. The effect of various Straight Run (SR) Distillate Blends in LCOs on SMORS yields. All values in mg/100 ml of fuel.

Volume Ratio SR/LCO	LCO ID	Pre-Stress SMORS		Post-Stress SMORS		Insol. Sed. Post Stress	
		Hi Acid SR-5A	Lo Acid SR-11	Hi Acid SR-5A	Lo Acid SR-11	High Acid	Low Acid
0/100	LCO-14	34	34	60	60	3	3
60/40	LCO-14	25	27	35	35	6	10
80/20	LCO-14	15	15	23	19	5	8
0/100	LCO-4	34	34	57	57	2	2
60/40	LCO-4	31	30	35	37	5	10
80/20	LCO-4	17	15	12	19	4	7

TABLE VII. Effect of Hexadecane as Diluent on SMORS Yields of an LCO. Aging conditions as in Table I.

Volume Ratio LCO-5/Hexadec.	mg SMORS per 100 ml LCO	Insol. Sed. (mg/100 ml)
100/0	96	11
80/20	129	23
50/50	148	20
20/80	147	23
0/100	0	0

TABLE VIII. Effect of 0.010 M Chloroacetic Acid on Pre-stressed SMORS Yields.

Sample	SMORS (mg/100 ml)
LCO-14	6
LCO-14 + Acid	23

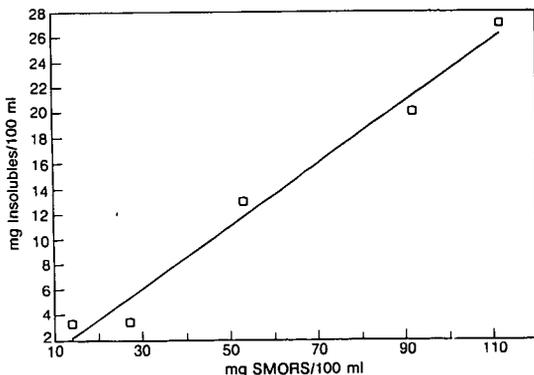


Figure 1. Correlation of weights of pre-stressed methanol extractable/hexane insolubles (SMORS) for 5 LCO samples with corresponding weight of product insolubles. See Table I for aging conditions. Standard error for each axis = $\pm 15\%$.