DESULPHURISATION OF COAL-OIL MIXTURES BY ATTRITION GRINDING WITH ACTIVATED IRON POWDER*

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INTRODUCTION:

Industrial progress and life itself inseparably depend on the quality of resources of water, land, and in particular, the air which we breathe. Air pollution, therefore, is of primary public concern and in all industrialized nations various steps are being undertaken to keep the air clean.

One of the main culprits of air pollution are fumes and gases from the combustion of fossile fuels. The principal toxic constituents of combustion gases are Sulphur Oxides from the Sulphur contained in Coal and in Fuel-Oils, derived from high-sulphurous crude oils. Excessive pollution of Air with combustion gases containing these sulphur oxides is understandably increasing with population growth, urbanisation and industrial expansion. No wonder, therefore, that in the United States, the 90th Congress passed the Air Pollution Bill No. 780 late in 1967 and has authorized close to a half billion dollars for a three-year program to combat Air Pollution. One of the points of this bill is for the U. S. Department of Health, Education, and Welfare to conduct Research on fuel beneficiation, leading to the elimination of Sulphur Oxides emission into the atmosphere.

To control air pollution caused by fumes and gases from combustion of high-sulphur fossile fuels, two basic approaches can be made:

1. To clean the combustion fumes and gases from Sulphur Oxides at their generation source prior to the release into the atmosphere;

2. To reduce the sulphur content of the fossile fuels BEFORE their combustion.

This short presentation is in the scope of the second approach, and I am attempting to show an economical, new way to remove Sulphur from Coal-Oil Mixtures.

I am fully aware that the experimental data presented herein is not conclusive and many questions remain to be answered by conducting of more detailed Research and Development work. This future work, however, should follow-up the present feasibility study in which, as it is given in the title of this lecture, organically bonded sulphur

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is being substantially removed from a Coal-Oil mixture by attrition grinding with activated powdery Iron.

Metals such as Iron, Nickel, Copper, Tin, Bronze, Lager Metal, etc. are capable to scavenge organically bonded sulphur from hydrocarbon type lube-oils under condition of friction. This has been well known for many decades.

For example, a lubricating oil which still contains some organically bonded sulphur because of insufficient refining, in use, very soon starts to show sludge formation. This sludge always analyzes for metallic sulphides.

It appears, therefore, that under high frictional forces occurring during the lubricating process in spite that the reactive surfaces of the contacting metallic surfaces are rather small and separated by a lubricating film, nevertheless, in time the organically bonded sulphur in the lubricating oil becomes slowly scavenged by the abraded minute metallic particles. In general, this phenomenon can be explained by the energetic preference of sulphur atoms to be bonded to metallic atoms rather than to carbon atoms.

As Metal Sulphides are insoluble in the lube-oil, this reaction proceeds further as the equilibrically preferred reaction.

When more favorable conditions are created, in which the used metal is in the form of a high surfaced fine powder, and its mixture with a sulphur containing oil-coal is most frequently and intimately attritionally mixed in a ball mill, it is obvious that in a shorter time a larger part of the organically bonded sulphur in the coal-oil mixture shall be scavenged by the metallic powder. The coal-oil mixture, from which molecules the sulphur atoms were abstracted, will under the reaction conditions partly depolymerise and partly polymerise, but in general a fluid fuel will result with a low sulphur content.

When this pasty reaction mixture is now diluted with a high boiling, good solvent, such as Tetralin* and centrifuged, the unreacted Metal and the Metal Sulphide having a relatively high specific gravity are easily separated from the reaction fluid, which now consists of an intimate dispersion of unreacted coal in an oily phase. After removal of the solvent, a low-sulphur, low-ash fuel results.

For the herein presented few exploratory experiments, the least expensive metal Iron Powder was used, although it might have been expected that Zinc, Tin, and Aluminum powders would perform better because of their higher atomic bond energy with Sulphur than Carbon.

However, the surface of Iron Powder easily becomes contaminated with reaction products with moist air, therefore, all commercial Iron Powders, even those which were made by hydrogen reduction have a partly oxidized surface. For that reason it was decided to prepare as much as possible a surface clean Iron Powder by the

* Tetralin - 1,2,3,4-Tetrahydronaphtalene - sp.gr. 60/60°F. = 0.971
m.p. = -30°C.; b.p. = 207°C.

following preactivation procedure:

A 0.1% benzene-absolute alcohol solution-dispersion of a mixture of three chemicals was percolated through the Iron powder.

This mixture consisted of a Cationic reducing wetting agent with an Organo-Tin compound doped with an Organo-Lead compound. (For patent reasons I do not feel free at this time to exactly identify these compounds.) After drying of the Iron powder in Nitrogen, it retained on the surface a plated-out, extra thin, metallic Tin film, whose weight was less than 0.05% of the weight of the Iron powder. Thus, what we really did was to deposit on the commercial Iron powder of a thin Tin-plate which, as we could observe under the microscope, was tenaciously adhering to the Iron powder surface even after the Iron powder was mixed into the coal-oil paste. This composition was applied with the expectation that the Tin plated Iron surface will initiate a Sulphur scavenging reaction, reminiscent of Melamid's Oil-Molten Tin cracking experience. The Tin plating of the Iron powder also appeared to prevent conglomeration of the Iron powder in the course of the grinding process.

Certainly, further considerable work should be done to explore how this really works and whether better wetting agents and activators can be found for that purpose. The use of radioactive tagging elements such as tritium and Fe_{59} incorporated into the wetting-activating compounds may elucidate their action.

EXPERIMENTAL:

I wish here to emphasize that the following presented herein few experiments should not give the impression that there is already on hand a developed method for Desulphurisation of Coal-Oil Mixtures. This is only a Feasibility Study in which I am only tentatively showing that by Attritional Grinding of a high-Sulphur containing paste made by solublizing Coal in Mineral Oil with a Sulphur Scavenging Metal such as inexpensive Iron powder, a quasi-metathetic reaction substantially appears to occur; this leading to a low-in-sulphur fuel, while producing Iron Sulphide as a commercially desirable by-product.

In order that this new method becomes inexpensive and practical, it should perform already at temperatures not much higher than 275°C.

Also the mixing-grinding reactor residence time should not be longer than 5 - 10 minutes. The reaction should also proceed preferably without the use of hydrogen because this requires high pressure working conditions. Hydrodesulphurisation is a too costly process for making a fuel only.

Finally, this new process should not produce appreciable amounts of low boiling volatiles resulting from high temperature decomposition of the oil and coal; this necessarily requiring a costly post-distillation step.

Only then, we may expect that the total production costs of a BTU shall be low enough to make it a practical desulphurisation method, competitive with the presently suggested H-oil process, which is using catalytic, high pressure hydrogenation of mineral oils.

Keeping all these considerations in view, for this limited feasibility study I have arbitrarily selected a conservative set of reaction constants, leaving for future much more extensive R & D work to find more efficiently working conditions:

The grinding time was five minutes at the grinding temperature of 250°C.

The grinder, equipped with a venting valve, was the well-known Union Process Company's Research Model Attritor No. 01.

This model has a grinding tank with a capacity of 750 cc. and delivered capacity of 200 - 400 cc.

To work at the intended high temperatures of 250 - 275°C., it was specially equipped with electrical wire heating and proper Teflon gasketing.

As grinding aids, steel balls of 15 mm. diameter were used.

The obtained from a supplier coal was predried and preground to an average 100 mesh. It was prepared from a high volatile coal grit, mined in the Mathies Mine in Washington county, near Pittsburgh, Pennsylvania. Its analysis after drying and grinding was:

Total Sulphur Content		1.70%	(of this, pyrite sulphur analyzed at 0.2%)
1.	Moisture	0.10%	
2.	Volatiles	39.00%	
3.	Fixed Carbon	55.00%	
4.	Ash	5.90%	
		100.00%	

The Iron Powder was a Niagara 100 mesh grade from the Pyron Company, a subsidiary of AMAX. It was an almost 100% pure hydrogen reduced Iron.

A constant weight ratio of 1:1 of coal powder to the solubilizing-grinding oil was kept in all experiments. At room temperature, depending on the physical and chemical properties of the used oil, the resulting mixture was a soft to firm paste. At the reaction temperature of 250°C. all these pastes were still thixotropic fluids evolving some volatile fumes; this again depending primarily upon its IBP and the composition and volatility of the used oil. The Fuel Oil No. 6 fumed the most because of its lowest IBP of only 489°F.

For our experiments we have selected <u>four</u> grades of grinding oils:

1. A high napthenic, low in aromatics oil: Tufflo 6094 from Sinclair Oil Company. This oil analyzed: Aromatics - 8% and total sulphur - Less than 0.001%

2. A high aromatic oil: Mobilsol 66 from Mobil Oil Company. This oil analyzed: Aromatics - 95% and total sulphur - only 0.4%

3. A high aromatic oil: Aromatic RFC Extract and Concentrate from Enjay Chemical Company. This oil analyzed: Aromatics - 88% and total sulphur - 1.30%

4. A typical Fuel Oil No. 6 from Humble Oil and Refining Company. This oil analyzed: Aromatics - 65% and total sulphur - 2.60%

It is evident from the above and Table I, which gives a more complete analysis of these four grinding oils, that two highly aromatic oils were used, but one with a low and the other with a relatively high Sulphur content.

A third oil, Tufflo 6094, which is very low in aromatics and sulphur-free, was tested. It was interesting to test such an oil for its solubilizing power for the coal powder and consequently to find out what relatively the percentage of sulphur removal from the coal will result when dispersed and solubilized in such a poorly solvatizing oil.

Finally, for practical reasons a typical Fuel Oil No. 6 (Bunker Oil C) was included. This, first to establish its solubilizing power for a coal, and at the same time to tentatively find out whether our new process can substantially reduce the Sulphur content in such a coal-oil mixture to the desired below one percent.

Thus, with one type of a high volatile coal and four grades of grinding oil, four double basic experiments were run as follows:

Each grinding oil and the Coal-Iron powder were mixed: One batch while only using the agitator without the steel balls in the Attritor No. 01; the pairing batch was made with the steel balls. For this twin experiment all other conditions of time, temperature, and amount of ingredients, etc. were identical.

The results of these eight typical experiments are presented in Table II.

PROCEDURE:

Before their discussion I wish to detail the experimental procedure applied for any single run:

In a separate stainless steel one liter beaker, equal weight parts of the before described dried coal powder and the oil at a temperature of 100°C. were spatula mixed until a uniform paste resulted. To this paste a calculated amount of freshly activated Iron powder was admixed.

For each experiment the Iron powder was calculated on the basis of the average Sulphur content in the 1:1 oil-coal mix, sufficient to fully scavenge the Sulphur giving FeS. From this mixture a small known sample was removed and held back for analysis. When Steel Balls were used, these balls put into Attritor 01 up to about 25% of its volume; this while moving around the steel balls in the tank of the Attritor which was preheated to about 250°C. The also preheated to about 250°C. Coal-Oil-Iron Powder paste was added slowly--all while agitating the balls, thus filling-up all the free space between the balls until the total filled volume was about 75% and the average charge was 250 grams. When no steel balls were used, a steel double scraper with a tank wall tolerance of one millimeter was attached to the agitator and again the Attritor's tank was filled up to its 75% volume with the same Coal-Oil-Iron Powder mixture.

In all experiments, as indicated before, the volume of the scraper equaled the used volume of the steel balls.

The mixing time was, as before, 5 minutes while the reaction temperature was kept at 250°C. which, occasionally when steel balls were used climbed up to 275°C.--this mainly due to frictional heat.

After the reaction, the mixing and heating was discontinued and while hot the mixture was strained from the grinding balls (whenever they were used) and cooled to a temperature of about 150°C.

Four graduated 100 ml. centrifuge tubes were in the meantime filled to a half mark with Tetralin heated to 160°C. Into these tubes, while well mixing up to the 100 ml. mark the 150°C. hot, Coal-Oil-Iron powder reaction product was filled and all of the four tubes were centrifuged.

The centrifuge tubes were of the 3011-F45 type as depicted in Thomas Catalogue on page 221 with constricted neck and tampered bottom graduated from 0 to 1 in 0.05 ml., from 1 to 3 ml. in 0.2 ml., from 6 to 10 ml. in 0.5 ml., and 10 to 100 ml. in 1 ml. divisions.

The used centrifuge was the Explosion-Proof, International Model 2-EXD, as depicted in Thomas Catalogue on page 185. The centrifuging head for the tubes was the 2943-A15 type--each holding simultaneously four 100 ml. tubes, described above. The centrifuging speed was about 2100 rpm.

The centrifuge was not heated and centrifuging time was kept in all experiments at 5 minutes, while the centrifuging temperature fluctuated from the initial 150°C. to about 120°C. at the end due to intermittent cooling-off.

After centrifuging we could notice in the tubes four poorly visible layers:

1. In the bottom tip the unreacted blackish hard residue, which could be identified as Iron Powder, partly contaminated with Iron Sulphide.

2. On top of it, a black soft layer, identified as Iron Sulphide, partly contaminated with Coal particles.

3. On top of it an Oil-Tetralin-Coal deep brown viscous layer.

4. The upper top was a rather clear brown Oil-Tetralin solution.

Our main interest was to analyze the two upper liquid layers on its sulphur content, which was done in the following way:

When still hot the two upper layers were carefully decanted. Tetralin was added to the tube, well shaken, and again centrifuged. Afterwards, the upper liquid was again carefully decanted from the tube and this procedure was repeated once more. Thus, finally on the bottom of the centrifuge tube we had a Tetralin wet mixture of unreacted Iron Powder mixed with Iron Sulphide and sulphur-rich insoluble in Tetralin polymerisates. This Residue was carefully collected into a beaker, twice washed with Hexane and dried. From

this black powder the Iron particles as much as possible were magnetically removed and the remaining powder analyzed for Sulphur in a Parr Bomb by the usual $BaSO_4$ gravimetrical method.

In all eight experiments we found a Sulphur content almost matching the Sulphur loss in the analyzed desulphurised oil-coal mixture.

The upper two layers from the centrifuges were mixed together with the Tetralin washings of the two lower layers, and Tetralin was distilled off from a small flask at about 200 - 210°C.

Finally we got a highly viscous, almost pasty, brown-black residue containing more or less suspended fine particulate coal; this depending upon the used grinding oil.

This residue was analyzed in a Parr Bomb for total sulphur. The results are presented on Table II.

In addition to these eight experiments a ninth experiment was made, in which the not activated Iron powder was used with the Coal-Fuel Oil No. 6 mixture. The comparative results are shown on Table III.

DISCUSSION AND CONCLUSIONS:

From the results shown on Tables II and III, we can tentatively make the following deductions:

1. Attritional grinding of a powdery high bituminous coal dispersed in a heavy mineral oil with Iron powder effected in five minutes at a temperature as low as 250°C. gives a higher degree of total sulphur removal than by conventional mixing. While for a straight mixing operation the Sulphur removal from three Coal-Oil mixtures averaged only 22%, attritional grinding with the same activated Iron Powder gave under otherwise identical working conditions a Total Sulphur removal as high as 53%.

2. Attritional grinding of a 1:1 dispersion of a high bituminous coal in Fuel Oil No. 6 with a non-activated Iron Powder and a specially activated Iron Powder gave a comparatively higher degree of Sulphur removal for the activated Iron Powder of 56% against 44% for the former.

3. For best Sulphur removal from Coal, the dispersing oil should contain predominantly aromatic compounds. This is shown clearly in Table II where two dispersing oils, one with an 8% aromatic content (Tufflo 6094), the other with 95% aromatic content (Mobilsol 66), were used for the same Coal. The first gave only an 11% Sulphur removal; the second gave 57% Sulphur removal.

4. The Sulphur removal from two Coal-Oil mixtures--the first being Mobilsol 66 which has a low Sulphur content of 0.4%, the second RFC Extract containing a triple percentage of Sulphur of 1.30%, give a similar percentage of removal of about 50%. This appears to imply that the Sulphur can be substantially removed not only from the Oil but also from the Coal, again provided that the Oil is of a highly aromatic type.

5. Mixtures of a Coal Powder, analyzing it at over one percent of total sulphur with a commercial Fuel Oil, which contains as high as 2.6% of organically bonded sulphur, can be desulphurised by the herein presented Attritional Grinding Method, while using a specially activated Iron Powder giving a down to less than one percent of Total Sulphur Fuel mixture.

FUTURE WORK:

The author believes that in R & D Work this process can be improved. This can be done by finding more favorable processing conditions. In particular, it is expected that by applying a higher reaction temperature and possibly increasing processing time over 5 minutes a higher degree of Sulphur removal can be attained.

It is also hoped that better Iron activators can be found--this may help in arriving at a lower in Sulphur Coal-Oil Fuel.

Further exploration of this new approach to Coal-Oil Desulphurisation appears worthwhile also for economical reasons. This because the expected processing conditions are rather mild, and the equipment for Grinding, Centrifuging, and Solvent Stripping are well developed and already available on an industrial scale. The high price of Sulphur, which by the presented method is produced as a by-product, should also contribute considerably to the lowering of processing costs.

TABLE I - PROPERTIES OF GRINDING OILS

Type of Grinding Oil	Tufflo 6094	Mobilsol 66	RFC Extract	Fuel Oil No. 6
Producer	Sinclair	Mobil	Enjay	Humble
Sulphur Content	None	0.4	1.3	2.6
Spec. Gr. 60/60°F.	0.9177	1.1050	1.054	0.969
Viscosity SSU at 100°F.	880	160	320	170
Viscosity SSU at 210°F.	190	38	62	35
Flash Point COC - °F.	425	385	405	180
ASTM Vac. Dist. (Cor. to Atm.)				
IBP	610	638	556	489
10%	780	697	644 (5%)	596
50%	821	724	776	927
90%	870 (95%)	793	1097	Cracked 971°F.
FBP	882	819	1126	Yield 62%
Clay/Gel Analysis				
Aromatics	8.0	95.0	88.0	65.0
Naphthenes + (Paraffin)	52 + (40)	1.0	10.0	12 + (8)
Polar Material	None	4.0	0.5	3.0
Asphaltenes	None	None	1.5	12.0
Carbon Type Analysis				
Aromatics Carbons	None			
Paraffinic Carbon	43			
Naphtenic Carbons	57			

TABLE II

Used Grinding Oil	Tufflo 6094	Mobilsol 66	RFC Extract	Fuel Oil No. 6
Analyzed total Sulphur content in the oil-coal mixture prior to the addition of the Iron Powder and before processing	0.85	1.05	1.50	2.15
Analyzed total Sulphur content in the oil-coal mixture after only mixing in the Attritor 01 without the steel balls	0.80 (or a reduction in "S" content of 6%)	0.80 (or a reduction in "S" content of 24%)	1.20 (or a reduction in "S" content of 20%)	1.70 (or a reduction in "S" content of 21%)
Analyzed total Sulphur content in the oil-coal mixture after attritional grinding with the steel balls	0.75 (or a reduction in "S" content of 11%)	0.45 (or a reduction in "S" content of 57%)	0.80 (or a reduction in "S" content of 47%)	0.95 (or a reduction in "S" content of 56%)

REMARKS:

In all experiments we could detect in the Residue, described in the text of this presentation, corresponding values of Sulphur which were scavenged with the Iron Powder.

TABLE III

Used Grinding Oil	Fuel Oil No. 6
Analyzed Total Sulphur Content in the Oil-Coal mixture after attritional grinding with the steel balls. The Iron powder was activated.	0.95 (or a reduction in "S" content of 56%)
Analyzed Total Sulphur Content in the Oil-Coal mixture after attritional grinding with the steel balls. The Iron powder was NOT activated.	1.20 (or a reduction in "S" content of ONLY 44%)