SOYBEAN OIL, NO LONGER JUST FOR COOKING by Brandon Weeks, Dr. Paul Worsey, Kurt Kosman, Daryl Andershock, Rock Mechanics and Explosives Research Center University of Missouri-Rolla, Rolla, MO 65409-0660

ABSTRACT

Several derivatives of soybean oil are currently manufactured and sold on the open market. Of these, the use of methylsoyate as a direct fuel substitute in diesel engines has been thoroughly researched and practically applied. The use of this product as a fuel gave rise to the idea of using a similar substitution in ANFO blasting agent. The Missouri Soybean Merchandising Council has sponsored a three-year research program. The project is funded for the purpose of opening up of new markets for Missouri soybean products.

Successful preliminary testing has been completed using raw soy oil, methylsoyate, and fully refined salad oil at UMR with detonation velocities and energies similar to ANFO. Work is currently being concentrated on the less processed oils to minimize production costs.

As oil prices rise and resources are depleted, soybean products should become competitive with fuel oil. It is hoped that the technology is ready for commercial production in advance of this scenario. Some advantages of soybean oils include: we don't have to rely on foreign sources, it's a renewable resource, and environmentally sound. Unlike traditional fuels, soybean oil does not evaporate, it's cleaner and acts as an anti-caking agent.

INTRODUCTION

Farmers meet many challenges to their goal of profitable soybean production. The Missouri Soybean Merchandising Council (MSMC) is a farmer controlled and financed organization responsible for funds received from the farmers gross sales (0.5%) which are used for soybean marketing and research. Past research efforts under this program focused on increased yields. However, for farmers to reap the benefits of increased yield, there must be increased demand for their product, otherwise increased production will result in a lowering of prices. Traditional markets appear to be saturated and new markets must be sought. Therefore, the Rock Mechanics and Explosives Research Center (RMERC) of the University of Missouri-Rolla (UMR) intends to open a new market for soybean oil for the MSMC.

The RMERC explosives engineering group proposed to replace the fossil fuels in explosives with soybean oil, a renewable resource. Currently, mining and construction are crucially important to the economy of this country. For example, quarrying alone is a 12 billion-dollar industry in the US. To excavate rock a vast amount of blasting agents and explosives are required, over 2.5 megatonnes (5.5 billion pounds) per year in the continental US alone (USBM). Of this, 97% is ammonium nitrate - fuel based. The fuels used in blasting agents and explosives are predominantly diesel oil and kerosene, which represents 5 to 6% of the mixture by weight, totaling approximately 113 kilotonnes (250 million pounds) per year. This represents a sizable market that has not yet been explored and has huge potential for soybean products. In addition, the major explosives companies have regional manufacturing facilities in Missouri, close to the source of production.

Soybeans produce a high-quality protein meal of up to 1800 lb./acre, which is normally used as livestock feed. Organic extraction provides, as a side product, the highest volume of oil produced from any agricultural crop. Soybean oil can initially be processed into methylsoyate by adding base and methanol, or into crude degummed by adding water which removes phosphatides or lechitin from raw vegetable oils. The crude degummed oil is then treated with alkalis to remove any free fatty acids from the oils. From here the oil can be deodorized and sold as salad oil (Figure 1).

Soybean oil, because of its properties, has great potential to replace diesel fuel in ANFO. We believe that by mixing soybean oil, or the mixture of soybean oil and diesel with ammonium nitrate, better quality explosives can be produced. Although, we have no knowledge of any previous attempt to use soybean oil as a diesel substitute in ANFO, significant research using soybean oil as a direct substitute for diesel fuel in internal combustion engines has been performed (Adams et al., 1983; Clark et al., 1984; Pryde, 1983). They have showed that soybean oil is a good substitute of diesel based on energy produced. However, the use of soybean oils as a diesel substitute in combustion engine generated some problems such as coking and trumpet formations on injectors, oil ring sticking, and thickening of lubrication oil that has come into contact with the soybean oil. In 1992, Lambert Airport (St. Louis) successfully used soy diesel for their maintenance vehicles by overcoming the preceding problems. Obviously an ANSoy explosive will not encounter the complications faced by the internal combustion engine, and the actual implementation of a soy diesel is further indication of successful ANSoy product possibilities. Soybean oil actually provides sufficient energy for the new ANSoy explosives. For a quick comparison, No. 2 Diesel has 9320 Kcal/L (140,000 Btu/gal) where soybean oil has 8654 Kcal/L (130,000 Btu/gal) and a 1:1 ratio mix of No. 2 diesel and soybean oil has 8996 Kcal/L (135,142 Btu/gal). This is an indication that soybean oil is a comparable product. Research indicates that using a mixture of diesel and soybean oil may have superior explosive properties.

Other products over the years have successfully been used as fuels in ANFO including carbon black, gasoline, used engine oils, aluminum, and nitromethane. In fact the first ammonium nitrate blasting agent was made using lamp black (Blasters' Handbook, 175ed., Du Pont). Diesel is the most common now because of its intimate contact with the AN prill and low cost.

RESEARCH PROGRAM

The ultimate goals of the proposed research are to investigate the use of soybean oil as a substitute for fuel in ammonium nitrate based explosives and to produce a marketable explosive based on soybean oil fuel, which is superior to those currently available. A time period of three years was estimated to finish the work on a part time basis. During this first year, an explosive mixture has been formulated for testing and demonstration. The second year will be used to increase the quality of the mixture and to develop a product suitable for manufacture. The third and final year will be dedicated to transferring the technology, and introducing the product on the market. The first year's work comprises: calculating ANSoy-Oxygen balance and theoretical energy for the most powerful mixture of ANSoy, mixing batches of ANSoy, and testing for velocity of detonation, sensitivity, energy, and performance vs. diameter of the charge. The results will then be compared to ANFO. The first year's work will be concluded with the manufacturing of

sufficient amounts of ANSoy for demonstrating reduced scale tests at the UMR Experimental Mine and/or a local quarry. The demonstration tests will be conducted for the council and interested manufacturers, and will be both instrumented and videotaped. It will allow us to show ANSoy's abilities for a potential industrial partner that can take the product from a research and development stage to the market. The second year's work includes refining the product for the blasting industry. The work will comprise: increasing the quality of the ANSoy mixture, defining manufacturing characteristics (effect of increased viscosity etc.), the quantitative analysis of ANSoy explosives, and field scale testing. An industrial partner will be sought during the later part of the year. The third year's work will comprise transferring the technology to industry, manufacturing on a full production scale, and field application in conjunction with an explosives manufacturer.

TESTING TO DATE

The initial contract was started in May of 1996. The results presented were obtained in the first nine months of year one. ANSoy blasting agents were first produced on a relatively small scale. Four soybean products, methylsoyate, salad oil, crude degummed, and raw soybean oil provided by the Missouri Soybean Merchandising Council were mixed from 5% to 8% in 50 gm of AN. The blasting agents were initiated with 8gm pentalite stingers. Power from these four different mixtures were recorded by measuring the degree of indentation of witness plates. These were the final tests performed with the salad oil and crude degummed soybean oils. Crude degummed oil was omitted from any further testing because of the high amount of water used in its processing and salad oil worked very well but was dropped because of the higher cost. VOD tests were conducted using 75 mm (3 in.) PVC tubing surrounded by 150 mm (6 in.) PVC (Figure 2). The void between the two pipes was filled with concrete to simulate a confined bore hole. The concrete/PVC tubes were 610 mm (2 ft.) long and held 2.2 Kg (5 lb.) of ANSoy blasting agent. Methylsoyate, raw, baked raw, and ANFO were all shot using 8 gm stingers. The baked product was derived by heating the ANSoy mixture in an oven at 100C overnight. Mixing of the soybean compounds with AN behave different with fuel oil with the exception of methylsoyate. Methylsoyate mixes well within a matter of hours while the raw compound takes many days. Since the raw soybean oil is the cheapest and theoretically most energetic, we are concentrating tests on this product and fuel impregnation rate tests were conducted. A two kilogram batch of 6.5% raw ANSoy mixture (oxygen balanced, figure 3) was made and 50 gm samples were shot every 24 hours. A witness plate was used to measure the power of the explosive. Underground blasting tests are in progress at UMR's experimental mine. Rounds incorporating 45mm (1 ¾") holes have already been blasted in V cuts and slabbing shots in conjunction with Mining 350, a senior level blasting class. In these tests a direct comparison was made between ANSoy and ANFO. These are being scaled up to full rounds. We are currently monitoring long term caking studies that are proving to be very good qualitatively. This test is conducted by letting the ANSoy product cycle from OC to 40C three times a day with ANFO as a standard for comparison. A standardized test is being developed to quantify the degree of caking.

RESULTS

Although RMERC is only a quarter of the way into the research program, the results have been more than just promising in fact, very exciting. Methylsoyate, crude, salad oil, and crude degummed in 50 gm AN all fired successfully, but the crude degummed had the weakest indentation on the witness plate. The results of these tests are displayed in figure 4 (note: 6.35mm (¼")

aluminum witness plates were used for these tests, subsequent tests used 6.35mm (¼") steel plates). Of the three-inch ID samples all went with the exception of raw soy oil. We consequently found that the raw needs several days of time to fully penetrate the prill. VOD results of the three soybean product mixes were comparable and surprisingly, better that ANFO: ANFO 3265m/s (10712 fps), baked raw 3305m/s (10843 fps), methylsoyate 3848m/s (12625 fps), and raw 3350m/s (10991 fps). Theoretical energy has been calculated for both ANSoy and ANFO as a comparison. Standard enthalpy calculations using heats of formation at standard temperature and pressure give values of 887 cal/gm for ANSoy and 916 cal/gm for ANFO. The value for ANFO being close to that traditionally quoted. The fuel impregnation tests have also been completed using the raw soybean oil. Between the first and fourth days of mixing, there is very little indentation on the witness plates. After five days there is a noticeable difference with a quadrupling of witness plate deformation (Figure 5). This phenomena has been verified by microscope studies and is due to a combination of the viscosity of the oil and the macrostructure of the prill. It is perceived that the slow penetration rate into the prill is an important hurdle to overcome. However, with the industry slowly moving away from truck mixed powder to premixed bulk truck (due to similar but shortened time frame problems with diesel), the penetration problem can be overcome simply by mixing the material well in advance. Viscosity modifiers are currently being investigated to change the characteristics of the raw oil so that the fuel may enter the prill within a day or less. Underground shots have also proved to be very successful in the dolomite rock at the UMR experimental mine. Pneumatic loading is identical to ANFO although the odors are not as pungent, and in fact for those who do not keep their mouths shut, the taste is far less offensive. We are looking forward to large-scale quarry shots

ADVANTAGES:

One of the biggest problems with ANFO is the evaporation of the fuel when stored over a long period of time. This leads to quality control problems because batches will have a different amount of fuel oil due to evaporation. Caking can also occur if temperature conditions are cycled above 32.2 C (90 F) or below -17.7 C (0 F) (Explosives and Rock Blasting, Atlas Powder Company, 1987). In the ANFO product, diesel fuel impregnates the solid ammonium nitrate matrix forming a near homogeneous distribution of the fuel with the ammonium nitrate crystals. The high vapor pressure of diesel fuel allows some mass transfer of the fuel oil to occur at the surface of the ammonium nitrate prill which can also leads to serious caking problems and reduced performance of the ANFO product. Soybean oil is a potential solution to these problems, because of its low vapor pressure. The oil adsorbed on the surface of the prill theoretically prevents direct contact between adjacent prill. ANSoy has shown negligible oil evaporation even when stored at 100C over a period of three days. No evaporation means a uniform product, even when stored under adverse temperature conditions over a prolonged period.

Soybeans are a renewable resource and the United States is the largest producers of soybeans, 49.22 million metric tons, so we do not have to rely on foreign fossil fuels or soybean crops. As far as the EPA is concerned, soybeans are biodegradable. This should be an advantage for misfired shots or disposal of excess blasting agents as you can return them to the field as fertilizer. Better fume characteristics have been observed pre and post blast using ANSoy which may provide a better fume classification for use underground with the virtual elimination of sulfur oxides. As a spin-off to our current work, we are evaluating the possibilities of developing a water-resistant ANSoy product, as baked ANSoy has a far superior water resistance than ANFO. This was observed when trying to clean one of the beakers used to bake the product. The baked prill did not dissolve even when kept underwater for two days. Separate studies of the polymerization of soybean oil as coatings for other uses are currently underway on the UMR campus.

SUMMARY

Soybean oils have proved to be a viable alternative in diesel engines. Our work has also proven these products to be excellent alternatives to fuel oils in AN blasting agents. The economics at this time is the only obstacle keeping ANSoy from competing on a one for one basis with ANFO. Currently the ANSoy product is calculated to be 5% more expensive than ANFO. If the advantages are figured in with the price we believe that ANSoy can be a more cost-effective product for many operations.

BIBLIOGRAPHY

Adams, C.; Peters, J. F.; Rand, M. C., 1983, "Investigation of Soybean Oil as a Diesel Fuel Extender: Endurance Tests", Journal of the American Oil Chemists' Society, v 60, pp. 1574-9.

Atlas Powder, 1987, "Explosives & Rock Blasting", Maple Press, Dallas TX.

Bailey, A.E., 1979, "Bailey's Industrial Oils and Fats", ISBN 0-471-83957-4.

Beauregard, Lawrence G., , "Non-food Uses of Soybean Oil", Chem. and Ind., no 1, pp. 18-21.

Clark, S. J.; Wagner, L.; Schrock, M. D.; 1984, "Methyl and Ethyl Soybean Esters as Renewable Fuels for Diesel Engines", Journal of the American Oil Chemists' Society, v 61, pp. 1632-8.

Drury, F.C., 1984, "The Effect of Gulf Coast Ammonia Prices on the Cost of Midwest Ammonium Nitrate", Journal of Explosives Engineering, Vol. 1, No 5, pp.33-35.

Du Pont, 1980, "Blasters' Handbook 175ed.", E. I. Du Pont de Nemours & Co., Wilmington, DE.

Erickson, D.R., 1995, "Practical Handbook of Soybean Processing and Utilization", ISBN 935315-63-2.

Pryde, E. H.; 1983, "Vegetable Oils as Diesel Fuels: Overview", Journal of the American Oil Chemists' Society, v 60, PP 1557-8.

Snyder, J. M.; Frankel, E. N.; Warner, K.; 1986, "Headspace Volatile Analysis to Evaluate Oxidative and Thermal Stability of Soybean Oil. Effect of Hydrogenation and Additives", Journal of the American Oil Chemists' Society, v 63, pp. 1055-8,.

US Bureau of Mines, 1994, "Mineral industries Surveys, Consumption of Industrial Explosives and Blasting Agents", Annual Review 1994, 5 pages.