TECHNOLOGY FOR ADVANCED LIQUEFACTION PROCESSES:
COAL/WASTE COPROCESSING STUDIES

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PROJECT OVERVIEW AND INTRODUCTION:

The efforts in this project are directed toward three areas: (1) novel catalyst (supported and unsupported) research and development, (2) study and optimization of major operating parameters (specifically pressure), and (3) coal/waste coprocessing.

The novel catalyst research and development activity has involved testing supported catalysts, dispersed catalysts, and use of catalyst testing units to investigate the effects of operating parameters (the second area) with both supported and unsupported catalysts. Several supported catalysts were tested in a simulated first stage coal liquefaction application at 404°C during this performance period. A Ni-Mo hydrous titanate catalyst on an Amocat support prepared by Sandia National Laboratories was tested. Other baseline experiments using AO-60 and Amocat, both Ni-Mo/Al_2O_3 supported catalysts, were also made. These experiments were short duration (approximately 12 days) and monitored the initial activity of the catalysts. The results of these tests indicate that the Sandia catalyst performed as well as the commercially prepared catalysts. Future tests are planned with other Sandia preparations. The dispersed catalysts tested include sulfated iron oxide, Bayferrox iron oxide (iron oxide from Miles, Inc.), and Bailey iron oxide (micronized iron oxide from Bailey, Inc.). The effects of space velocity, temperature, and solvent-to-coal ratio on coal liquefaction activity with the dispersed catalysts were investigated. A comparison of the coal liquefaction activity of these catalysts relative to iron catalysts tested earlier, including FeOOH-impregnated coal, was made.

The potential for reducing pressure in coal liquefaction using various combinations of dispersed catalysts and donor solvents are being investigated. To date, the efforts have focused on microautoclave experiments. The results of the microautoclave efforts are reported in the "Liquefaction Chemistry and Kinetics: Hydrogen Utilization Studies" project discussion. Future plans are to extend the microautoclave efforts to semi-batch and continuous tests.

As part of the U.S. Department of Energy (DOE) Fossil Energy program, the Pittsburgh Energy Technology Center (PETC) recently initiated research in coal waste coprocessing. The objective of this project is to explore and facilitate development of processes that will economically convert, into liquid fuel feedstock, a combination of any or all of the following; coal, rubber, plastics, heavy oil, waste oil, and paper. The effort to date has centered on the combined processing of coal and heavy oil (coal-oil coprocessing), coal and plastics, and a smaller effort with coal and rubber. The initial effort with coal and plastics has focused on the reactivity of coal/plastics mixtures and the operability of processes that utilize these feedstocks. This paper summarizes the coal/waste coprocessing efforts. The early stages of this work have been presented at a Symposium at the American Chemical Society National Meeting[1] and recently at the Ninth Annual Consortium for Fossil Energy Technical Meeting[2].

EXPERIMENTAL SECTION

Materials Liquefaction experiments were conducted with -200-mesh Black Thunder mine coal (Wyodak-Anderson seam, Campbell County, WY). High-density polyethylene (PE), melting point 135°C, density 0.96 g/mL, was manufactured by Solvay Polymers. Polystyrene (PS), melting point 95°C, was manufactured by BASF. Poly(ethylene terephthalate) (PET), melting point 215 C, density 1.4 g/mL, was manufactured by Hoescht Celanese as IMPET EKX-105. All plastics were supplied to PETC by HTI, formerly HRI, as 3.2-mm (1/8-in) extrudates. A mildly hydrogenated (9% hydrogen) fluid catalytic cracking (FCC) decant oil, obtained as the 340-510°C (650-950 °F) fraction from run POC-1 on the proof-of-concept coal liquefaction unit at HTI, was used as a vehicle in the coal-waste coprocessing experiments. Aged Akzo AO-60 Ni-Mo/Al_2O_3 catalyst was obtained from run POC-1 at HTI.

Reactions Microautoclave reactions were conducted in 42-mL cylindrical, stainless-steel batch reactors constructed at PETC. The base conditions of the reactions were 2:1 hydrogenated FCC decant oil vehicle : coal-plastics mixture, one hour at 430°C, 7 MPa (1000 psi) cold hydrogen gas pressure, and 0.6 g aged Akzo AO-60 catalyst, although variations in time, temperature, and catalyst composition were also made. During workup, the reactor contents were sonicated in tetrahydrofuran (THF) for 30 minutes and subsequently filtered through a 0.45-micron filter under 40 psi nitrogen gas pressure. The THF soluble material was stripped of solvent on a rotary evaporator and re-extracted with heptane to produce a heptane soluble fraction. Conversion was calculated from the measured mass of insolubles adjusted for catalyst and coal mineral matter, based on the mass of plastic and MAF coal. The mass of the catalyst was also adjusted for the presence of entrained oil in the material as determined in a separate extraction step. The PE and PET plastics showed no significant solubility in either THF or heptane under the workup conditions used. PS did show appreciable solubility in THF, rendering those conversion calculations meaningless.

Semi-batch (batch slurry, flow-through gas) reactions were performed in a 1-L stirred-tank reactor system. The feed charge consisted of 350 g of slurry that typically consisted of a 2:1 ratio of vehicle:feed with 30 g aged AO-60 catalyst. The experiments were done at temperatures of 430-460°C under 17.5 MPa (2500 psi) hydrogen gas pressure flowing at a rate of 1.9 L/min (4 SCF/h). The products were characterized in terms of gas yield and composition, solubility in heptane and THF, and 450°C conversion [conversion of all material distilling above 450° C (850° F), including MAF coal, plastics, and 450°C+ oil, to material distilling below 450°C].

Continuous mode catalytic liquefaction experiments were conducted in a computer controlled 1-L bench-scale unit. The unit is a once-through system without recycle. A typical charge consisted of a vehicle:feed mixture of 70/30 at an overall slurry feed rate of 146 g/h. The catalyst, 35 g of aged AO-60, was contained in an annular basket surrounding the stirrer to simulate the action in an ebullated bed. The coprocessing experiments were done at reactor temperatures of 400-460°C under 17.5 MPa (2500 psi) of a 97% H_2 / 3% H_2S gas mixture flowing at a rate of 2.4 L/min (5 SCF/h). The products were characterized by distillation into three fractions - those boiling below 340°C (650°F), between 340-450°C (650°F-850°F), and above 450°C (850°F).

Gas Analyses Microautoclave reactor gas samples were collected at the completion of each run. Hydrogen consumption was calculated, based on the difference between initial and final (cold) gas pressure as adjusted for product gas composition. Semi-batch unit gas samples were collected once during the run (tail gas), and at its completion (flash gas). Hydrogen consumption was calculated based on the assumption that the tail gas sample was representative of the gas make throughout the run.

Viscosity Measurements Viscosity measurements were made to obtain data on feed mixtures in support of continuous unit operations. These measurements were conducted on a CANNON Model MV 8000 rotational viscometer equipped with an optional heating jacket and spindle capable of measuring viscosities as high as 500,000 cP at temperatures up to 260°C. The sample holder was loaded with 10.5 mL of material and tests were conducted over the temperature range corresponding to actual operating conditions. Viscosities were also measured over a series of sheer rates, again corresponding to unit operating conditions. Regressions indicated that the oil-coal-plastics mixtures are well represented as power law fluids, i.e. viscosity is proportional to shear rate raised to some power.

RESULTS AND DISCUSSION

Feed Slurry Rheology Studies The rheological properties of the feed slurry for coprocessing will be a significant factor in determining the pumpability and feed system requirements (e.g., pressure drop) of the slurry. Measurements of viscosity and flow properties will be used to develop a database to compare the feed requirements of systems using different types of hydrocarbon wastes.

The effect of plastic component type on viscosity was evaluated with HRI-L800 (a hydrotreated decant oil obtained from HTI, Inc.) oil as the solvent. Three major components were investigated: high density polyethylene (HDPE), polystyrene (PS), and polyethylene terephthalate (PET).

Figure 1 shows the effect of component type (including a commingled plastic mixture of 50% HDPE, 35% PS, and 15% PET) on slurry viscosity. The HDPE resulted in the highest viscosity, and the viscosity of the commingled system was intermediate between that of the HDPE and the PS systems. PET was not successfully tested, since it was not possible to obtain a single phase mixture with PET and oil. To successfully use PET a second plastic component, either PS or HDPE, has been required. It is unclear whether a synergy is observed with the commingled system with respect to viscosity. However, it is clear that a benefit is observed with the commingled system with respect to being able to obtain a single phase containing PET.

Figure 2 presents the effect of varying the relative amounts of coal and the commingled plastics mixture while maintaining a 70/30 oil-to-solids ratio. The HTI oil and Black Thunder (BT) subbituminous coal were used with the plastics mixture (HTI oil/BT/plastics) in these measurements.

As shown in Figure 2, increasing the plastics content at the expense of the coal results in higher slurry viscosities. Figure 3 shows the effect of commingled plastics addition in the oil/plastics (no coal) system. As expected, the viscosity increases with increasing plastics content.

In separate tests, no significant difference was observed between BT and Illinois No. 6 coal. However, there did appear to be a dependence of viscosity on solvent type. Differences were observed between use of North Slope ATB, Wilsonville V-1074 heavy distillate, and the HRI L-800 oil.

From continuous experiments that were conducted on the PETC bench-scale liquefaction units, two observations were made regarding the needs for pumping slurries containing plastics. The high viscosity of the mixture requires high temperature and head pressure during pumping. However, if the viscosity becomes too low and the feed rate is low, settling of the suspended coal becomes significant and plugging will occur.

Waste Coprocessing Reactivity Studies Microautoclave studies were conducted to determine the conditions required to convert the plastics, especially HDPE. At 430°C both PS and PET were easily converted to heptane soluble products. However, no significant conversion of HDPE was observed at this condition. Table I summarizes the results of the microautoclave tests. For the most part, the conversions observed in mixed plastics with coal systems indicated that the plastics were compatible with coal. There was one exception, however; it appears that the presence of coal (and in several cases an aromatic solvent) inhibited the conversion of HDPE. Only at higher temperatures was significant HDPE conversion observed in the presence of coal.

Experiments were also made with semi-batch reactors. For the most part, the observations from microautoclave experiments were also evident in the semi-batch reactors. The difficulty of converting HDPE was also observed in the semi-batch reactors.

Two separate continuous experiments (with 9 run conditions) on coal/waste coprocessing (over 100 hours) were successfully conducted on one of the PETC bench-scale units with Black Thunder subbituminous coal and commingled plastic. The major accomplishments of these experiments were determining the proper operating envelope for processing coal/waste slurries and confirming high HDPE conversion. In selecting the proper feed temperature, both high and low viscosity effects (refer to Task 1) had to be addressed. The catalyst used in the continuous tests was a supported NiMo on alumina, AO-60. It is worth noting that HDPE conversion was observed at elevated temperature with a hydrogenation catalyst (and no specific cracking catalyst). Table II summarizes the conditions used for the continuous experiments.

POC-Scale and Bench-Scale Coprocessing Product Analysis The HTI POC-2 (a proof of concept run of coal/waste coprocessing at HTI, Inc.) and CMSL-08 (a bench-scale test of coal/waste coprocessing at HTI, Inc.) samples have been subjected to an extensive suite of analytical techniques, with the goals of determining (1) what is the fate of the plastic materials; (2) how the presence of plastics and coal affects the processing of each of these components; and (3) whether the traditional measurements of process efficiency, such as conversion, are applicable to mixed coal-waste systems. Analyses include low voltage high-resolution mass spectrometry (LVHRMS), nuclear magnetic resonance (NMR), infrared spectroscopy (IR), potentiometric titration, and electron paramagnetic resonance (EPR) spectroscopy.

Low-voltage, High-resolution Mass Spectrometry LVHRMS results were obtained from POC-2 samples SP-3 (naphtha stabilized bottoms), SP-4 (atmospheric still bottoms), and SP-5 (vacuum still overhead) samples for run periods 36(coal-only), 43(coal+plastic), and 45(coal+rubber). The data follow a logical progression of increasing average molecular weight and degree of condensation and decreasing hydrogen-to-carbon ratio, as the sampling points varied from SP-3 (naphtha stabilized bottoms) to SP-4 (atmospheric still bottoms) to SP-5 (vacuum still overhead). The three SP-3 samples ranged in average molecular weight from 130 to 170, while the three SP-4 samples ranged from 195 to 215 and the three SP-5 from 220 to 230.

The most dramatic observation from the LVHRMS data is a dominant C_2-benzene peak in the spectrum of SP-3, period 43. This peak is more than twice as intense as the next most prevalent signal. It is attributed to ethylbenzene from depolymerization and hydrogenation of polystyrene in the plastics mix. The assignment is supported by analogous results from coupled gas chromatography - mass spectrometry analysis.

Nuclear Magnetic Resonance Spectroscopy NMR spectra were obtained for the SP-3 (naphtha stabilized bottoms), SP-4 (atmospheric still bottoms), and SP-5 (vacuum still overhead) samples for run periods 36, 43, and 45.

For a given run period, carbon aromaticity follows the sequence SP-3 < SP-4 < SP-5. In fact, the correlation is strong enough that none of the SP-5 samples has a carbon aromaticity less than any of the SP-4 samples, none of which exhibit carbon aromaticities less than any of the SP-3 samples. This is consistent with expectations of increased aromaticity as the distillation cuts become heavier. Within a given sample point, the carbon aromaticity always increases (or stays the same) in the order period 36 < period 45 < period 43. This is more likely related to the aromatic products of PS and PET plastic degradation, and to the presence of hydrogenated decant oil added as make up solvent in the coprocessing run periods.

Fourier Transform Infrared Spectroscopy FTIR spectra were recorded of the SP-27 (ROSE bottoms) product from periods 36 and 43. The results provide strong evidence of polyethylene in the ROSE bottoms product. The period 43 sample showed polyethylene aliphatic C-H and CH_2 bands at 2910, 2850, 1460 and 720 cm^{-1}. Based on period 43 results alone, it was not clear whether the bands were due to polyethylene or waxy material from the coal. However, these bands were much less prevalent in the period 36 product. A difference spectrum between the period 43 and 36 samples compared very well with the major bands in a neat polyethylene sample. These data do not indicate how much of the polyethylene is being removed, or whether the polyethylene that was removed had undergone any cracking. However, they do indicate that at least some of the polyethylene is not converting and is being removed in the ROSE extraction step.

SUMMARY AND CONCLUSIONS

Individually, plastics degrade as reported in the literature, and products rapidly hydrogenate to saturation. HDPE generally requires more severe conditions for conversion to solubles than either PS or PET. The traditional solvent extraction methods for evaluating coal conversion are not particularly appropriate for plastics. The feed PS was found to be soluble in THF. It is quite possible that in cases where no HDPE conversion was observed (by THF solubility analysis) that, in fact, the HDPE chain was broken down, just not sufficiently for solvent extraction.

Less hydrogen may be required to produce saturated products from plastics (if gas production can be minimized), since the average waste plastic stream is less aromatic than coal. However, under traditional liquefaction conditions, each C-C bond scission still consumes one molecule of H_2, because any olefinic products formed as a result of depolymerization rapidly hydrogenate to saturates. This is particularly true with PE, which tends to degrade randomly along the polymer chain.

In the two-component and multicomponent microautoclave tests, THF solubles could be reasonably well predicted from the behavior of the individual components under similar conditions. However, the heptane solubles were greater than that predicted by the assumption of individual behavior. This may be indicative of some type of synergistic behavior in coliquefaction of coal with plastics. Further work in this area will be done, including investigating the addition of polypropylene.

The viscosity of coal-plastics mixtures increases significantly as the plastics concentration increases. PE seems to have the greatest influence on viscosity. Higher temperatures were required to pump the mixture when the composition was raised from 25% to 50% plastics. Control of viscosity by control of temperature was the key to successful operation of continuous mode coprocessing. Future investigations in continuous operations of the effect of solvent type and plastics concentrations will be done.

DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

REFERENCES

1. Rothenberger, K.S., Cugini, A.V., Ciocco, M.V., Anderson, R.R., and Veloski, G.V., Am. Chem. Soc., Div. of Fuel Chemistry, Prep., Vol. 40(1), 38-43(1995).

2. To be presented at the 9th Technical Meeting of the Consortium for Fossil Fuel Liquefaction Science.

TABLE I: SUMMARY OF MICROAUTOCLAVE REACTION CONDITIONS AND RESULTS

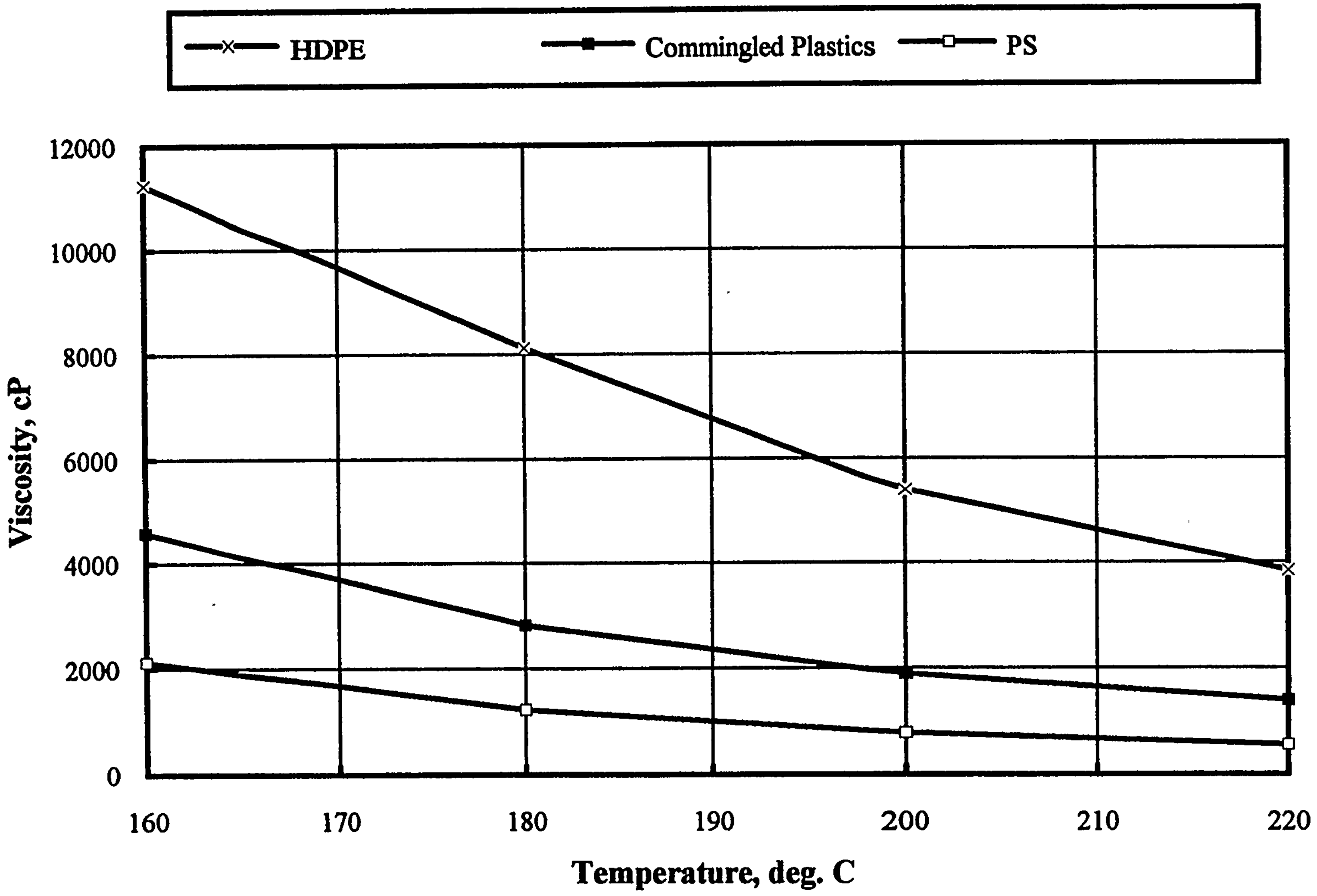
Experiment	Feed Mixture (%) Coal	 PE	 PS	 PET	Vh:F[1]	Catal	Time min.	Temp. (°C)	Conv. % THF	 Hept	H_2cons (mmol)
Single-Component Reactions											
I	100	0	0	0	2:1	AO-60	60	430	83	51	50
II	0	100	0	0	1:1	AO-60	60	430	-19	-19	28
III	0	100	0	0	2:1	AO-60	30	465	79	76	75
IV	0	0	100	0	2:1	none	60	430	94	77	N/A
V	0	0	100	0	2:1	AO-60	60	430	98	98	N/A
VI	0	0	100	0	2:1	AO-60	60	430	97	96	54
VII	0	0	0	100	2:1	AO-60	60	430	93	86	N/A
Two-Component Reactions											
VIII	33	67	0	0	1:1	AO-60	60	430	28	26	38
IX	50	50	0	0	6.6:1	HTO	60	430	36	27	41
X	50	50	0	0	6.6:1	HTO	60	430	34	24	39
XI	0	67	33	0	1:1	AO-60	60	430	36	36	N/A
XII	0	67	0	33	1:1	AO-60	60	430	35	35	46
Multicomponent Reactions											
XIII	70	15	10	5	2:1	AO-60	60	445	71	37	73
XIV	70	15	10	5	2:1	AO-60	120	445	48	13	N/A
XV	70	15	10	5	2:1	Fe-S	120	445	67	26	N/A
XVI	50	25	16	9	2:1	AO-60	60	430	65	57	54
XVII	50	25	16	9	2:1	AO-60	60	430	63	56	49

[1] 2:1 Vehicle:Feed (Vh:F) represented 6.6g vehicle : 3.3g feed; 1:1 Vh:F = 3.3g vehicle : 3.3g feed; 6.5:1 Vh:F = 6.6g vehicle : 1g feed

Table II. Summary of Continuous Test Conditions

Test:	I	II	III	IV	V	VI	VII	VIII	IX
Coal:	Black Thunder	Black Thunder	Black Thunder	Black Thunder	Black Thunder	Black Thunder	Black Thunder	Black Thunder	Black Thunder
Wt% Coal:	22.5%	22.5%	22.5%	22.5%	15.0%	22.5%	20.0%	15.0%	22.5%
Wt% Plastics:	7.5%	7.5%	7.5%	7.5%	15.0%	7.5%	10.0%	15.0%	7.5%
Wt% HDPE	50%	50%	50%	50%	50%	50%	50%	50%	60%
Wt% PS	35%	35%	35%	35%	35%	35%	35%	35%	40%
Wt% PET	15%	15%	15%	15%	15%	15%	15%	15%	0%
Temperature (degree C):	430	430	430	430	430	430	430	430	460
Feed Rate(g/h):	198	142	162	167	117	146	146	146	146

Figure 1. Effect of Plastics Type on Viscosity



Commingled Plastics Mixture: 50% HDPE, 35% PS, 15%PET

Figure 2. Effect of Coal to Plastics (C:P) Ratio on Viscosity

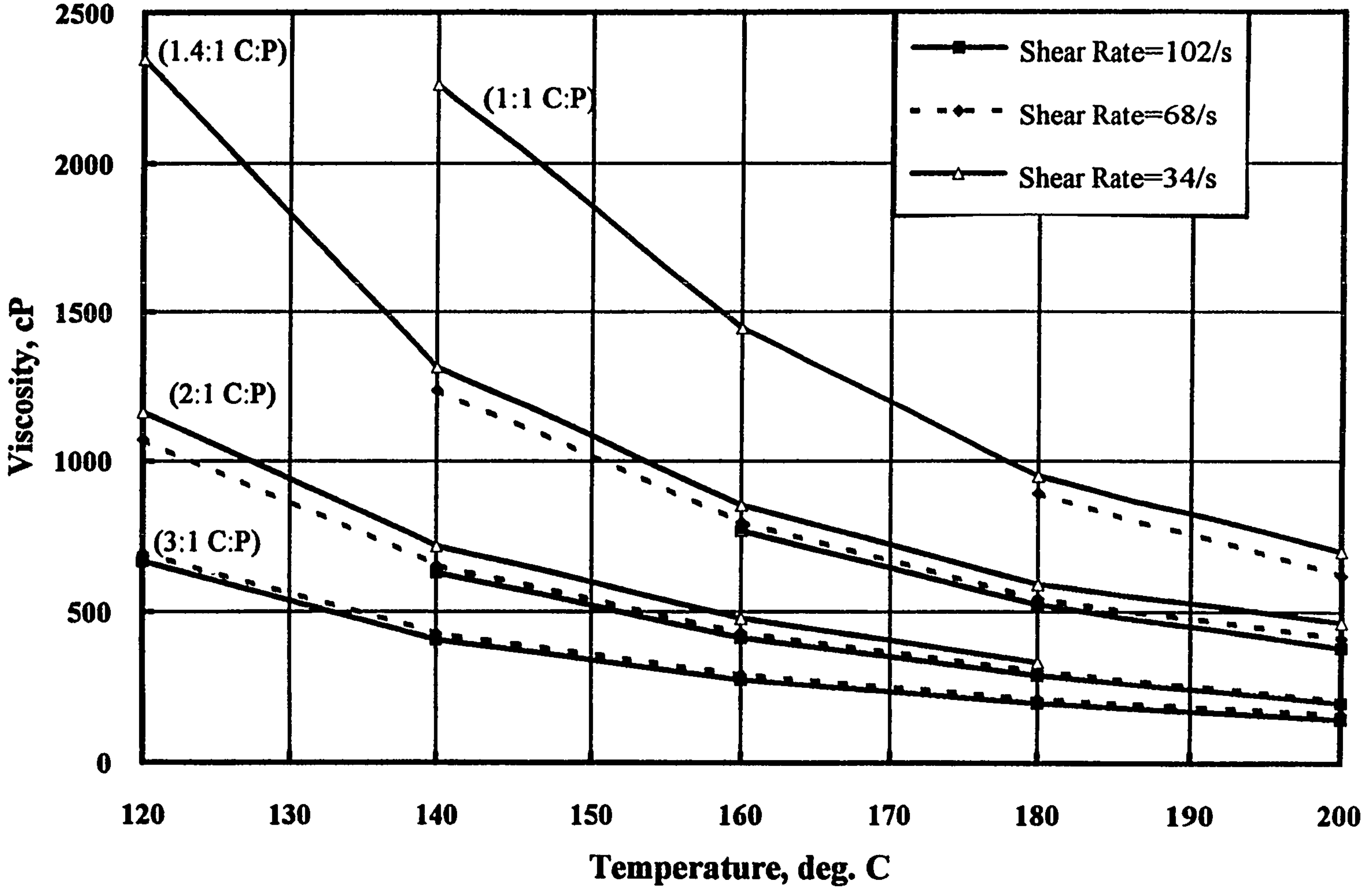


Figure 3. Effect of Plastics Content on Viscosity using HRI L800 Oil and Commingled Plastics