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Project Summary

Development of Methods for the Stabilization of Pyrolytic Oils

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In this study, capillary gas chromatographic, liquid chromatographic, and gas chromatographic mass spectrometric procedures were developed for analyzing pyrolytic oils. The major components of the oils and the chemical reactions that cause polymerization were identified. Some of the major components identified in pyrolytic oils were ethanol, 1-butanol, guaiacol, naphthalene, eugenol, acetaldehyde, and 4-hydroxy-3-methoxystyrene.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Annually, large amounts of agricultural waste are produced in the United States. The disposal of this waste material is becoming an increasingly more difficult and expensive matter. Agricultural wastes are largely lignocellulosic in chemical nature. Pyrolysis is one approach for converting agricultural, forestry, and municipal wastes to useful energy of chemical forms.

The products resulting from the pyrolysis of the organic fraction of solid wastes include noncondensable gases, liquids, and a solid residue of carbonaceous material or char. Analysis of the evolved pyrolytic gas stream indicates the presence of hydrogen, carbon dioxide, carbon monoxide, methane, ethane, and ethylene. The individual gas compositions very with pyrolysis conditions. The solid material remaining after pyrolysis is an impure carbon and ash. The liquid fraction of pyrolytic oil contains organics and water.

The pyrolytic oils are mixtures of neutral compounds and strong and weak acids. The oils are viscous, sticky liquids at room temperature. The pyrolytic oils appear to oxidize and/or polymerize on standing. During this study, methods were developed for determining the chemical composition of the pyrolytic oils, and attempts were made to stabilize the pyrolytic oils against whatever changes they undergo.

Methods and Results

The pyrolytic oil distillate was analyzed on an Aerograph 1440 gas chromatograph with a flame ionization detector. The conditions were: a 10-ft by 1/8-in. stainless steel column packed with 2% OV-210 on 100/120 mesh Supelcoport F-01409*; oven temperature program, 50° to 225° at 10°C per min; helium flow rate, 30 ml/min. Peak identifications were made by noting the enhancement of peak size when known substances were chromatographed with the distillate. Peak assignments are given in Table 1.

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

The oil distillate was also analyzed on the Varian 3740 capillary gas chromatograph under the same conditions.

Stabilization studies were conducted to determine mechanisms that lead to polymerization of pyrolytic oils. When a chromatogram of a pyrolytic oil sample was compared with one made 9 months later, the observation was that isoeugenol and 4-hydroxy-3-methoxystyrene peaks disappear on aging of the oil. This finding substantiates our suggestion that cationic, chain-reaction polymerization or oligomerization is responsible for substantial increases in viscosity of the pyrolytic oils on aging. Also discussed is the potential of the pyrolytic oils as a source of chemicals. The full report lists chemicals present in pyrolytic oil and their prices as reported in Chemical Marketing Reporter.

In an earlier EPA-supported study, "Pyrolytic Oils" (EPA-600/2-80-122), methods were developed to separate oils into fractions containing phenolics, polyhydroxy neutral compounds, neutral compounds of a high degree of aromaticity, and volatile acidic compounds. The results of these methods will be useful in determining full potential of pyrolysis for production of chemicals and fuels.

The full report was submitted in fulfillment of Grants Nos. R-804440010 and R-804440020 by Atlanta University, Atlanta, GA, under the sponsorship of the U.S. Environmental Protection Agency.

Table 1. *Typical Pyrolytic Oil Distillates*

Sample	*m/e (Relative Intensity %)*
1-Heptanol	*29(38), 31(25), 41(96), 42(56), 43(68), 54(68), 55(100), 56(30), 69(56), 70(96), 73(66), 84(25), 99(7), 100(8)*
2,3-Dimethylphenol	*31(11), 36(30), 43(17), 45(12), 54(14), 56(10), 79(17), 80(11), 81(17),93(17), 107(75), 122(100)*
2,4-Dimethylphenol	*31(2), 94(10), 107(60), 121(30), 122(100)*
2,6-Dimethylphenol	*36(6), 43(8), 55(6), 80(25), 82(22), 94(20), 107(40), 122(100)*
Naphthalene	*36(13), 43(25), 54(6), 67(5), 104(7), 128(100)*
2-Methoxy-4-methyl phenol	*31(16), 35(44), 45(41), 54(14), 55(30), 56(14), 57(14), 59(30), 68(20), 69(20), 70(30), 80(22), 81(18), 95(58), 123(100), 138(100)*
Veratrole	*29(4), 41(18), 52(12), 63(10), 64(12), 65(12), 93(38), 123(100), 138(97), 139(10)*

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The complete report, entitled "Development of Methods for the Stabilization of Pyrolytic Oils," (Order No. PB 82-108 150; Cost: $9.50, subject to change) will be available only from:
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