PYROLYSIS OF LIGNOCELLULOSIC MATERIALS. PHENOLIC CONSTITUENTS OF A WOOD PYROLYTIC OIL[1]

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ABSTRACT

Liquid pyrolytic products have been examined qualitatively and quantitatively for the presence of phenols. The liquid was solvent-extracted and examined by gas chromatography/mass spectrometry. The phenolic fraction contained phenol, o-cresol, guaiacol, m,p-cresol, 2,4-dimethylphenol, 4-methylguaiacol, 4-ethylguaiacol, 4-propylguaiacol, eugenol, and isoeugenol. The total phenolic content was found to be 13.34% gravimetrically, but only 3.1% could be accounted for by chromatographic means, indicating the presence of a large proportion of nonvolatile, possibly polymeric material.

Keywords: Pyrolysis, phenols, gas-liquid chromatography, mass spectrometry.

INTRODUCTION

The forests of the United States represent a renewable resource requiring intelligent use and management. This is illustrated by the fact that recent studies have indicated that by the year 2020, assuming current relative pricing, the demand for roundwood in the United States could be up to 28 billion cubic feet per year, which represents a little more than doubling of the demand during the next fifty years (USFS 1975). It has also been found that the biological potential of the forest lands of the United States is 29.1–34.6 billion cubic feet per year (Spurr and Vaux 1976). It can be seen, therefore, that the demand is rapidly approaching the ultimate supply. Bearing this in mind, there is increasing interest in the maximum utilization of our forest productivities. Logging and other processing steps generate considerable residues, which up until this time have been discarded as waste or simply not used. For example, the commercial forest lands of East Texas provide an annual harvest of 475 million cubic feet and produce as much as 5 million tons of logging residues annually (Soltes 1979). This material, which has largely been ignored in the past, is now being considered as a resource in its own right.

Increased utilization of residues in the future may come as a result of several

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TABLE 1. *Material and energy balance, Tech-Air Process (Knight 1976).*

		Material balance	Energy balance	BTU/lb.
Input:	Pine bark/sawdust	100	100	8,755
	Air and moisture	49	—	
Output:	Char	23	35	11,000–13,500
	Oil	25	35	10,000–13,000
	Gas	68	22	200–500 BTU/SCF
	Water	33	—	—
	Losses	—	8	—

conversion processes under current development. One probable process is the thermal degradation of lignocellulosic material, which is presently being viewed with a great deal of interest, as a possible route to alternate energy sources and chemical raw materials (Knight et al. 1976; Soltes and Elder 1978). Thermal degradation routes to chemicals from wood have undergone several cycles in the chemical and energy markets, especially since the advent of petroleum sources. In assessing woody material for energy purposes, it should be borne in mind that to utilize biomass in its usual unaltered form would require a changeover from the present combustion technology, which is based on fossil sources in the form of coal, fuel oil or natural gas, to a system that would be compatible with the much lower density woody material. Thermal degradation, in general, may offer a solution to this problem through the reforming that occurs as a result of heating. Thermal degradation may take a variety of forms, including: liquefaction, in which organic material is converted in a reducing medium, primarily to liquid, but also to solid and gaseous fractions; gasification, in which organics are converted to hydrogen, carbon monoxide, carbon dioxide, and water by partial combustion; and pyrolysis, which converts organics to solid, liquid, and gas by the action of heat in the absence of air or oxygen (Molton and Demmitt 1978). The amounts of solid, liquid, and gaseous fractions formed in these methods have been found to be quite dependent on the process variables, as are the constituents within

TABLE 2. *Properties of Tech-Air oil (Lin 1978).*

Property	Result
Density	1.1415 g/ml
Water content	9.7–14.0%
Heating value	9,100–11,934 BTU/lb.
Solubility (wt. %)	
Water	39.7%
Acetone	99.6%
Methylene chloride	93.5%
Toluene	slight
Hexane	slight
pH	2.9
Filterable solids (wt. %)	0.3%
Acidity (milliequivalents per gram of oil)	0.64

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                              WATER INSOLUBLES

                                     │
                                     │  ether extraction
                                     │
                                     │
  Residue 1────────────┴────────────── Solution 1
                                                │
                                     HCl extraction │
                                                │
                 ┌──────────────────────────────┐
  Ether Layer 2                         Solution 2
         │                              bases and
         │                              amphoteric compounds
         │  sodium hydroxide extraction
         ┌────────────────────────────────┐
  Ether Layer 4                         Solution 4
         │                      saturate with CO2
         │                      extract with ether
         │                              │
         │                 ┌────────────┐
         │          Ether Layer 5    Solution 5
         │                 │            │
         │                 │            │
  Neutrals            Weak acids    Stronger acids
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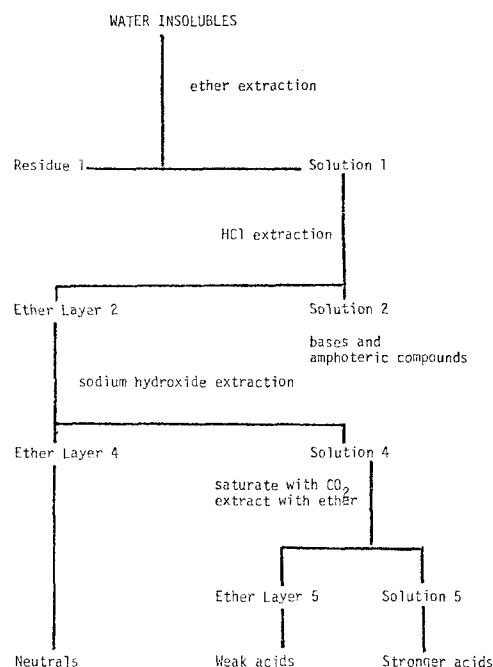
FIG. 1. Extraction sequence for phenolics from Tech-Air oil (Shriner et al. 1964).

each of these three large compound classes. Pyrolysis will be the only process considered in this paper. In addition to the energy component that may be derived from thermal degradation products, there is an opportunity for the derivation of various chemicals that could be of more potential value than the fuels. This study qualitatively and quantitatively examines the phenolic content of a pyrolytic oil.

The material to be considered in this study is a liquid fraction from a demonstration scale pyrolytic plant. This fraction is a complex mixture of chemical species, but some similarities to the constituents of the original wood can be discerned. It has been found in previous work that phenolic-type compounds may account for up to one-third of the pyrolytic oil (Lin 1978).

METHODS AND MATERIALS

The liquid fraction that has been analyzed in this study is produced from a fifty-ton-per-day demonstration plant operated by the Tech-Air Corporation of Cordele, Georgia. The process is continuous in a porous, vertical bed and uses temperatures in the range of 600–1800 F. The demonstration plant is located in a wood yard, and the feed material is pine sawdust and bark waste generated from the sawmill. The real advantage of this system lies in the material and energy balances shown in Table 1 (Knight et al. 1976). It may be seen for the pine bark/sawdust mixture, the yields of products from the input feeds are 23% char, 25% pyrolytic oil, 68% noncondensible gases, and 33% water vapor. The total is greater than 100% because of the assimilation of nitrogen and oxygen, due to the use
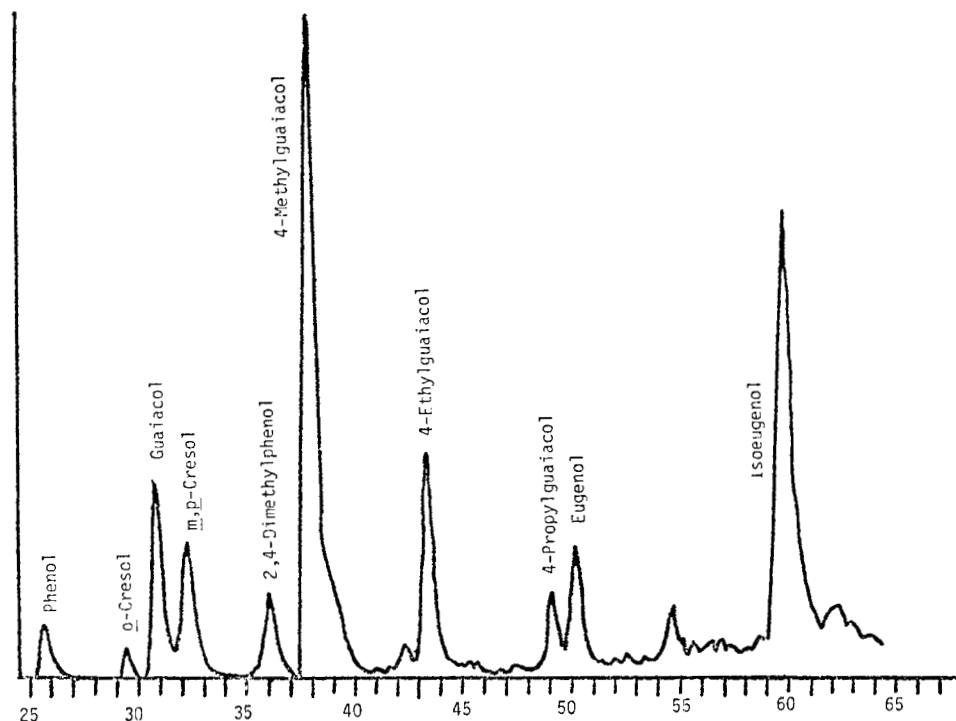
FIG. 2. Chromatogram of phenolic fraction from Tech-Air oil.

of some process air; in this way, the Tech-Air process is not a true pyrolysis. These yield levels will show some variation due to the type of input feeds and process parameters, but these levels are typical for wood residues. It may be seen that about 50% of the mass of the oven-dry input feed is converted to char and pyrolytic oil, while each of these fractions accounts for 35% of the original energy of the feed material, the noncondensibles account for 21.7%, and heat losses account for the rest. The relationship of interest lies in the fact that 70% of the energy content of the oven-dry feed material is found in about 50% of the mass, thus resulting in a concentration of the energy.

The conversion of biomass type material in this way provides advantages over conventional burning of wood waste. The BTU content of the char is found to be 11,000–13,500 BTU/lb and 10,000–13,000 BTU/lb for the oil as opposed to about 8620 BTU/lb for oven-dry wood. The converted material may be shipped by existing means available for liquids and solids, and circumvents the storage problems inherent with biomass. The liquid fraction that is to be analyzed in this study has the properties delineated in Table 2. Experience with the oil by previous workers (Lin et al. 1978) has indicated that we are dealing with a large complex mixture of components, and it was decided to begin the analytical efforts by separating the material by functionality, in an attempt to obtain a clean phenolic fraction.
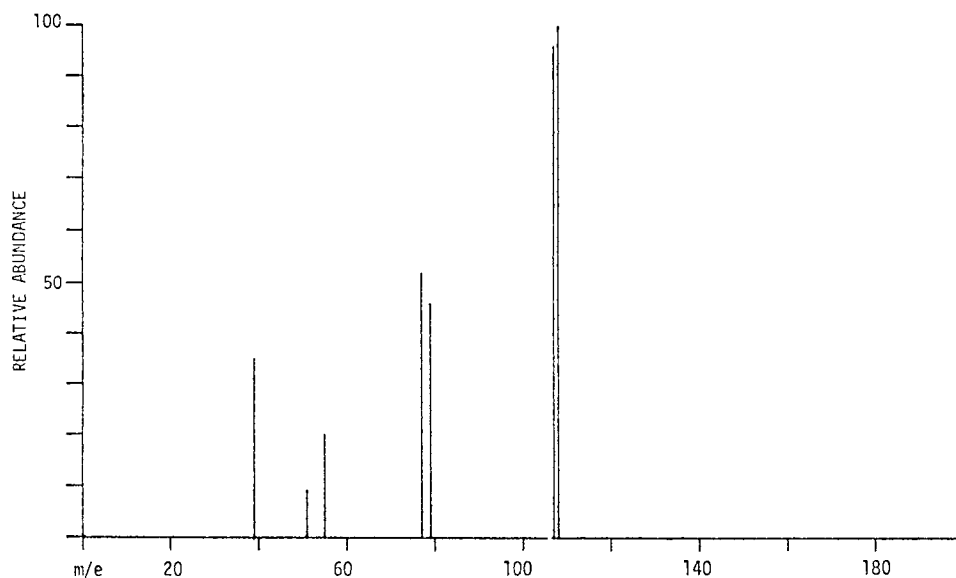
FIG. 3.   Mass spectrum of *o*-cresol.

ANALYSIS OF THE PYROLYTIC OIL

The extraction procedure began with a water wash to isolate the water solubles. Upon obtaining this fraction, the phenolics were removed according to an extraction sequence set forth by Shriner et al. (1964), and illustrated in Fig. 1. The water insolubles were washed with 75 ml of ether, and the ether insolubles (Residue 1) were filtered out. The ether solution (Solution 1) was next extracted with 5% hydrochloric acid. The acid solution containing the bases and amphoteric compounds was discarded, while the ether (Ether Layer 2) was retained. Ether Layer 2 was then extracted with 5% sodium hydroxide to give Ether Layer 4 and Solution 4. The ether layer was evaporated to yield neutral compounds. The aqueous solution (Solution 4) was cooled and saturated with carbon dioxide. The weak acids were then extracted with several portions of ether (Ether Layer 5), which was then evaporated to concentrate the weak acids that contained the phenols. The aqueous portion (Solution 5) was acidified and extracted with ether to yield the stronger acids.

Once the phenolic fraction was isolated, it was examined with gas-liquid chromatography, by use of a Tracor 560 gas chromatograph, equipped with a flame ionization detector. Helium was used as the carrier gas, with a flow-rate of 30 ml/min. The stationary phase was 10% OS-138/H_3PO_4/SP-1210 on 100/120 Chromosorb W-AW. The instrument was temperature programmed from 100–200 at 2 C/min with a four-minute initial hold. Preliminary runs were made to optimize the separation, and then the samples were submitted to interfaced gas-liquid chromatography/mass spectrometry for qualitative analysis. The instrument used was a Hewlett-Packard 5982A, with a quadrupole mass analyzer, a source temperature of 175–180 C and an electron energy of 70 eV. The resultant mass spectra
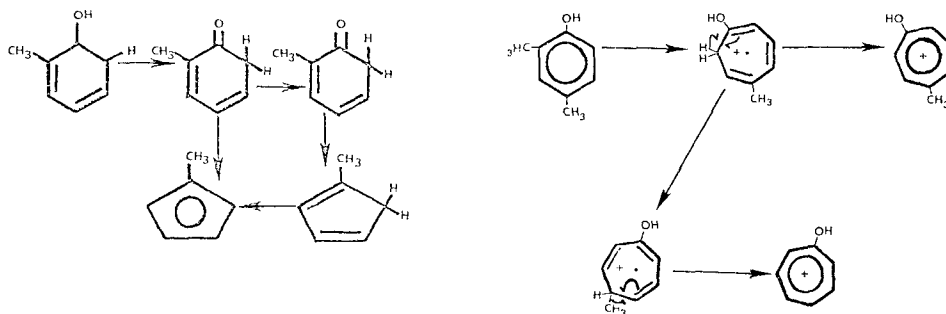
FIG. 4. Fragmentation mechanism of cresols.
FIG. 5. Fragmentation mechanism of dimethylphenol.

were compared with spectra found in the literature (Mass Spectrometry Data Centre 1974) to establish identification. These identifications were further verified by the addition of authentic reference compounds to the experimental solution, and by comparison of retention times.

Quantitative analysis was performed by use of guaiacol as an internal standard. An initial chromatogram was run with the experimental mixture, after which a known quantity of guaiacol was added, and the mixture was examined again. The differences in peak area were noted, equated with the amount of guaiacol that had been added, and all other components were determined on the basis of the mass per unit area of the guaiacol.
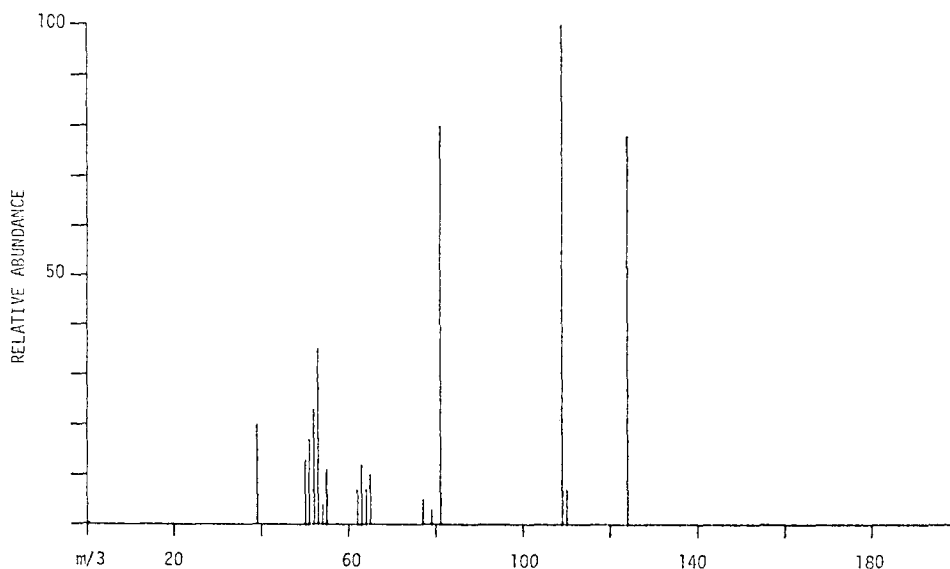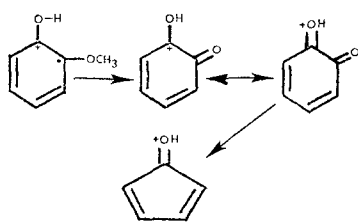

FIG. 6. Mass spectrum of guaiacol.

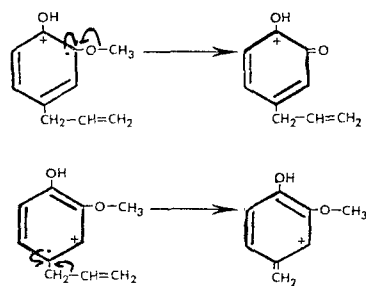FIG. 7.   Fragmentation mechanism of guaiacol.
FIG. 8.   Fragmentation mechanism of eugenol.

RESULTS AND DISCUSSION

The chromatographic analysis of the weak acid fraction that contains the phenols is shown in Fig. 2. The qualitative assignments that have been made are shown on the chromatogram. It was noted that the compounds in the mixture will align themselves into groups of similar fragmentation mechanisms, differing only by the presence or absence of a substituent group. For example, phenol and cresol show very similar fragmentation mechanisms, illustrated by the mechanism and mass spectrum for cresol (Figs. 3 and 4) (McLafferty 1973). The fragmentation of 2,4-dimethylphenol was found to be unique, and is illustrated in Fig. 5 (McLafferty 1973). The remaining compounds are all homologs of guaiacol, and are generally characterized by an alpha-cleavage of the methoxyl group (Figs. 6 and 7) (Kovacik et al. 1969). As the aliphatic side chain grows, however, it takes on more importance, as shown in the fragmentation mechanism and mass spec-
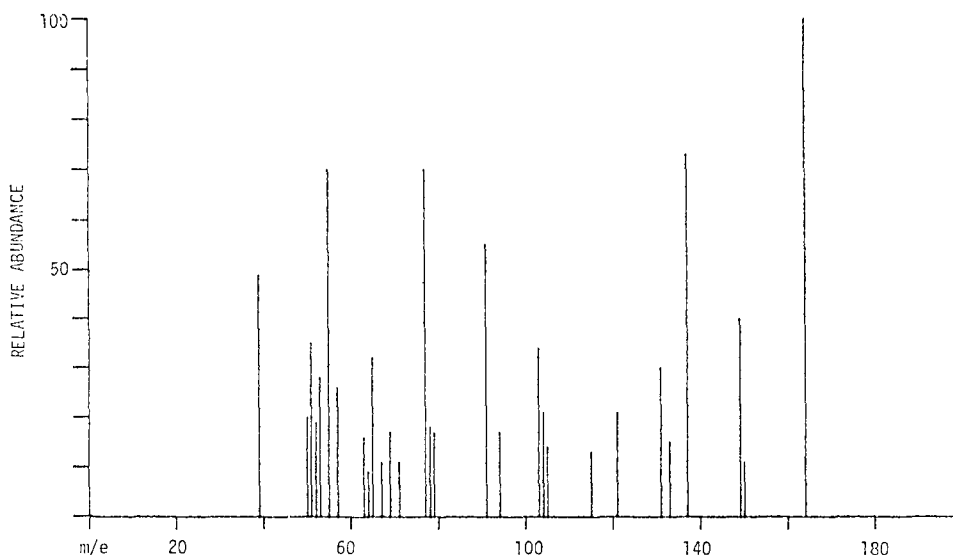

FIG. 9.   Mass spectrum of eugenol.

TABLE 3. *Absolute and relative retention times of phenolic components found in the Tech-Air oil.*

Compound	Retention time*	Relative retention time
Phenol	24.7	0.67
o-Cresol	28.5	0.77
Guaiacol	29.8	0.81
m,p-Cresol	31.3	0.85
2,4,-Dimethylphenol	35.1	0.95
4-Methylguaiacol	36.9	1.00
4-Ethylguaiacol	42.3	1.15
4-Propylguaiacol	48.1	1.30
Eugenol	49.1	1.33
Isoeugenol	58.8	1.59

* Minutes, conditions stated.

trum of eugenol (Figs. 8 and 9) (Kovacik et al. 1969). Absolute and relative retention times are illustrated in Table 3, and the quantitative results are shown in Table 4. Phenol was found to account for 0.21% of the original oil, o-cresol was 0.128%, guaiacol was 0.31%, m,p-cresol was 0.224%, 2,4-dimethylphenol was 0.073%, 4-methylguaiacol, the largest peak, was 0.769%, 4-ethylguaiacol was 0.24.1%, 4-propylguaiacol was 0.064%, eugenol was 0.425% and isoeugenol accounted for 0.680%. This indicated that 3.1% of the total oil may be accounted for with the chromatographic methods that have been described. On the other hand, the phenols account for an average of 13.34% of the total oil when determined gravimetrically; this indicates that about 75% of the phenolic fraction is nonvolatile and potentially polymeric. Additionally, the water-soluble material from the initial extraction of the pyrolytic oil was examined for phenols, and was found to be a very low amount in comparison with the phenols found in the insoluble fraction. It is interesting to note the similarity between the phenolic compounds found in the pyrolytic oil and the building blocks of the lignin molecules. The most graphic example lies in the series of guaiacols, which begins with guaiacol and progressively extends the aliphatic side chain to three carbons in length.

The attractiveness of the phenols is due in part to the uniformity of functionality

TABLE 4. *Quantitative analysis of phenolic components found in the Tech-Air oil.*

Compound	Percentage of total oil
Phenol	0.215
o-Cresol	0.128
Guaiacol	0.313
m,p-Cresol	0.224
2,4-Dimethylphenol	0.073
4-Methylguaiacol	0.769
4-Ethylguaiacol	0.241
4-Propylguaiacol	0.064
Eugenol	0.425
Isoeugenol	0.680
TOTAL	3.132

that the fraction has exhibited. Both the stronger acid fraction and the neutrals have been subjected to a cursory examination, and a large mixture of components is present in both, while the phenols have resulted in a very clean separation that contained only phenolic type compounds. This could be of particular interest in potential utilization schemes, which can use a variety of compounds, but with similar functionality and chemistry.

CONCLUSIONS

It is readily apparent from this study that single components present in this pyrolytic oil are present in such low concentrations as to preclude the isolation of any one particular chemical species. The effort that has gone into the phenolic fraction is primarily due to the clean separation that has been obtained by solvent extraction. The weak acid fraction only shows phenols present, while the other fractions have very complex mixtures. Any utilization opportunities would need to take advantage of this fact. Although the phenolic fraction is a mixture, all compounds are derivatives of phenol and would have the same type of chemical properties.

Efforts to utilize the phenols are continuing, with particular emphasis on novel adhesives that use the pyrolytic oil or an extract thereof as the phenol source for thermosetting adhesives. The question that must ultimately be answered is concerned with the economics of pyrolytic processing of material for chemical production as opposed to their derivation from petrochemical sources. Pyrolysis is an unknown economic quantity and under current economic constraints is probably not feasible, but for example, synthetic phenol prices have risen from $0.75/lb in 1973 (Chemical Economics Handbook 1978) to $0.35/lb in 1979 (Chemical Marketing Reporter 1979), which represents a 466% increase in cost. The information presented in this study has been intended to show technical, but not necessarily economic feasibility. In the past six years substantial changes have been made in the economics, availabilities, and attitudes toward fossil sources of chemicals and energy. If the past six years are any indication of what is to come in the future, the technology that has been studied in this paper could well have a practical impact, and pyrolytically derived phenols could become economically feasible. If petrochemical sources are depleted either naturally, through mining activities, or by political means, there could be drastic changes in which processes are realistic and which are not.

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