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Environmentally Compliant Vinyl Ester Resin (VER) Composite Matrix Resin Derived from Renewable Resources

SERDP Project WP-1755

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14. ABSTRACT

The feasibility of producing a sustainable, environmentally safe vinyl ester resin (VER) for military structural composite weapons systems was successfully demonstrated starting with low-cost lignin and glycerin waste streams. The synthesis of vinyl ester resin from lignin was conducted in four consecutive chemical reaction steps: Isolation of phenol from lignin via hydrolysis in supercritical water, Conversion of phenol to Bisphenol A, Synthesis of glycidyl methacrylate (GMA) from glycerin via conversion to glycidol followed by reaction with methyl methacrylic acid, and synthesis of vinyl ester resin via reaction of Bisphenol A with glycidyl methacrylate (GMA) eliminating use of highly toxic epichlorohydrin in the process. The successful program can provide a sustainable, environmentally safe source of vinyl ester resin monomer and other valuable chemical starting materials, starting from inexpensive, non-petroleum waste streams of lignin and glycerin.

15. SUBJECT TERMS
bisphenol A (BPA), bisphenol A-glycidyl methacrylate (BISGMA), glycidyl methacrylate (GMA), methyl methacrylate (MMA), Vinyl Ester Resin (VER),

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Abbreviations and Acronyms

AEM/S	advanced enclosed mast/sensor
BDMA	benzyldimethyl amine
BISGMA	bisphenol A-glycidyl methacrylate
BPA	bisphenol A
DCC	dicyclohexylcarbodiimide
DCM	dichloromethane
DMAc	N, N'-dimethylacetamide
DMF	N, N'-dimethylformamide
DoD	Department of Defense
EG	ethylene glycol
EPA	Environmental Protection Agency
FTIR	Fourier-transform infrared spectra
GC/MS	gas chromatography / mass spectrometry
GMA	glycidyl methacrylate
HAP	hazardous air pollutant
HCl	hydrochloric acid
HPLC	high-performance liquid chromatography
HPS	high-pressure systems
LC/MS	liquid chromatography / mass spectrometry
MA	methacrylic acid
MeOH	methanol
MMA	methyl methacrylate
NaOH	sodium hydroxide
NMR	nuclear magnetic resonance
PET	polyethylene terephthalate
RD	reactive diluent
R_f	retention factor
SESVER	sustainable, environmentally safe vinyl ester resin
SoN	statement of need
TGA	thermogravimetric analysis
TLC	thin-layer chromatography
TPA	terephthalic acid
UV	Ultraviolet
VARTM	vacuum-assisted resin transfer molding
VE	vinyl ester
VER	vinyl ester resin
QNA	QinetiQ North America

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1 Abstract

Environmentally Compliant Vinyl Ester Resin (VER) Composite Matrix Resin Derived from Renewable Resources

Objectives: The objective of this limited scope SERDP program was to demonstrate feasibility of producing a sustainable, environmentally safe vinyl ester resin for military structural composite weapons systems starting with low-cost lignin and glycerin waste streams.

Technical Approach: The synthesis of vinyl ester resin from lignin was conducted in four consective chemical reaction steps:

1) Isolation of phenol from lignin via hydrolysis in supercritical water,
2) Conversion of phenol to bisphenol A,
3) Synthesis of glycidyl methacrylate from glycerin via conversion to glycidol followed by reaction with methacrylic acid
4) Synthesis of vinyl ester resin via reaction of bisphenol A with glycidyl methacrylate, eliminating use of toxic epichlorohydrin. Published procedures were used for each step, in order to minimize danger, risk and time.

Results: During this program, the presence of phenol in lignin hydrolysis reaction products was confirmed at 5-10% yield. Substituted phenolics guaicol and catechol were also produced that can subsequently be converted to phenol to increase yield. Synthesis of bisphenol A from authentic phenol was achieved in >90% yield. Glycidyl methacrylate was synthesized via direct reaction of glycidol with methacrylic acid in >90% yield. Reaction of bisphenol A with glycidyl methacrylate produced vinyl ester resin in >95% yield. Environmental safety in each step was assured through use of approved equipment and safe working practices. Phase I results indicated that feasibility had been demonstrated and that work should continue to refine each intermediate step, scale up to larger quantities, and produce carbon-fiber reinforced vinyl ester resin composite components for military weapons.

Benefits: The successful program can provide a sustainable, environmentally safe source of vinyl ester resin monomer and other valuable chemical starting materials, starting from inexpensive, nonpetroleum waste streams of lignin and glycerin. This can enhance the independence of the United States from foreign oil.

2 Objectives

The prime objective of this limited-scope, phase I SERDP program was to demonstrate the feasibility of economically producing a sustainable, environmentally safe vinyl ester resin (SESVER) for military composite structures. These structures would be derived from bio-waste materials: lignin, recovered from wood wastes, and glycerin, recovered from biodiesel wastes. These abundant source materials are renewable, low-cost and independent of the food supply. A key environmental objective was to eliminate use of epichlorohydrin from the vinyl ester resin (VER) synthesis route. Elimination of hazardous styrene reactive diluent (RD) from the VER formulation was deferred for subsequent research.

2a. Criteria for Success

Criteria for this project's success included:
1) Isolation of phenol from lignin via hydrolysis in supercritical water at 400C/4000psi pressure or via flash pyrolysis of dry lignin in inert atmosphere.
2) Conversion of phenol to bisphenol A.
3) Synthesis of vinyl ester resin via reaction of bisphenol A with glycidyl methacrylate, thereby eliminating the use of toxic epichlorohydrin.
4) Synthesis of glycidyl methacrylate via two-step conversion of glycerin to glycidol (1, 2-epoxy-3-hydroxypropane) followed by direct reaction of glycidol with methacrylic acid in the presence of dicyclohexyl carbodiimide (DCC) dehydrating agent.

2b. Risk Reduction

Risk was reduced by utilizing previously published literature procedures during implementation of each intermediate synthesis step, including high-pressure hydrolysis of lignin. This practice minimized danger, risk and time required for completion of the experimental effort. Our successful completion of each individual chemical synthesis step provided critical information regarding the feasibility of isolating phenol from lignin and implementing a multi step phenol convertion into VER matrix resin for application to carbon fiber-reinforced VER composite structural components in military weapons systems. This successful achievement satisfied the SERDP statement of need (SoN) requirements to develop composite materials (and their constituents) for military use that are derived from renewable feedstocks using environmentally compliant processing and manufacturing techniques.

3 Background

3a. DoD Environmental and Regulatory Requirements Addressed

Use of composite materials for construction of DoD weapons platforms will approach 200 million pounds per year. VER is a low-cost resin that can be processed at ambient temperature using vacuum-assisted resin transfer molding (VARTM) into massive carbon-fiber-reinforced composite structures such as ship hulls and transportation vehicles. Since VER production is highly dependent on oil it is subject to fluctuating prices and limitations in supply. The continued viability of this strategic DoD weapons material is further jeopardized by the manufacture use of hazardous materials, epichlorohydrin and styrene.

Fiber-reinforced composites produced from VER have become the material of choice for marine applications, especially for next-generation U.S. Navy ships. VER is a low-cost material that can be processed to form a matrix of fiber-reinforced composites that are excellent construction materials for ship hulls, transportation vehicles, and many other military and commercial systems. VER is finding increasing application in the transportation, construction, marine, and wind energy industries. In 2000, over 60 million pounds of VER was sold in North America. Since then, the US Navy's need for VER has significantly increased. For example, the 500-ton deckhouse structure for the DDG 1000 is fabricated from carbon/VER composites. Current plans are for up to two ships per year with a total of 20 to 32 ships. The US Navy has recently used Derakane 510A brominated VER on the advanced enclosed mast/sensor (AEM/S) mast on the *USS Radford* (DD 968), LPD-17 masts, composite advanced sail, and the composite high-speed vessel, as well as the DDG 1000.

Vinyl ester composite matrix resins are formulated from VER, a solvent/reactive diluent (typically styrene), as well as additives to meet specific application needs. In general, VER has several advantages over other polymers. For example, toughened and brominated VERs produce cured resins with higher strengths than polyesters and are lower in viscosity than epoxies. This low viscosity is critical for fabricating large ship structures by vacuum infusion processing. Fiberglass-reinforced VER composites are preferred for many topside applications where low detectability and radar transmission are important. Recent advances in compatible sizings, however, have enabled the use of stiffer, stronger, carbon fiber reinforcements for VER composites.

As a result of its increasing use for military weapon systems, VER is considered a strategic DoD resource. However, the resin, as currently manufactured, has three important disadvantages:

1. VER is currently synthesized from petroleum feedstock, so its production is dependent on oil. Consequently VER is subject to rapid price fluctuations and its supply might become unreliable and limited in times of oil shortages.
2. VER is synthesized from epichlorohydrin, a known environmental hazard that produces high acute toxicity from inhalation, oral, and dermal exposure. It is also classified by the EPA as a Group B2: probable human carcinogen.

3. Styrene monomer, a major RD component of VER, is an environmentally hazardous substance, being volatile, flammable, and toxic. In addition to being an irritant, styrene can affect the gastrointestinal and central nervous systems, and has been categorized by the EPA as being a hazardous air pollutant (HAP) and possibly carcinogenic for humans.

To ensure the continued viability of this strategic VER material, it was essential to

- Develop VER synthesis routes that are not dependent on petroleum,
- Develop VER synthesis routes that eliminate the use of epichlorohydrin, and
- Develop resin formulations that do not contain hazardous components such as styrene (postponed to follow-on research)

To ensure sustainability of the new processing route, starting materials should be derived from readily available renewable resources. Furthermore, the resultant VER must retain the desirable economic and performance characteristics of the current products.

3b. Previous Related Research

In this subsection, the biowaste source materials are described briefly, followed by more detailed information on the process steps and the product VER.

Biowastes

Lignin: Hundreds of millions of pounds of waste wood pulp are generated in this country each year, largely as residue from pulp mills. Lignin, a polymeric aromatic material in woody materials, constitutes about one-third of the wood pulp. It can be readily extracted from the waste material at low cost and then converted to phenols by pyrolysis.

Glycerin: Currently, annual biodiesel production is being scaled up to hundreds of millions of gallons. Glycerin, an unwanted byproduct from biodiesel production, can be converted into glycidyl methacrylate, an intermediate required for VER synthesis.

3c. The QinetiQ North America (QNA) Approach

In this limited-scope SERDP Phase I program, QinetiQ North America (QNA) has successfully demonstrated the feasibility of economically producing an environmentally compliant VER composite matrix from low-cost renewable starting materials lignin and glycerin. As illustrated in Figure 1, these substances were recovered from biowastes, using processes that were independent of petroleum and coal supplies.

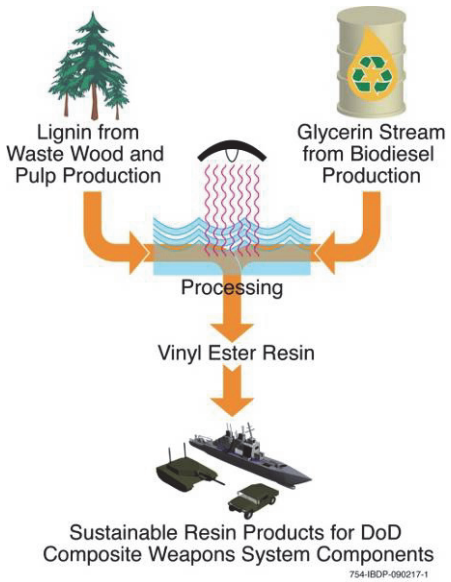


Figure 1 - The QNA concept for epichlorohydrin-free manufacture of vinyl ester resin (VER) from renewable resources

The resulting sustainable, environmentally safe vinyl ester resin (SESVER) will meet the specifications for VER-based DoD composite weapons system components that include Naval ship hulls and Army combat vehicles. The limited scope program has generated critical experimental data that had been needed to assess the viability of the proposed SESVER reactant and product materials, paving the way for additional research for process refinement in a multiyear program. Successful completion of additional research should result in a sustainable, economical, environmentally compliant and reliable source of VER for the fabrication of critical DoD VER-based composite weapons system components using a low-cost vacuum-assisted resin transfer molded (VARTM) process. Steps to commercialize the process would subsequently be initiated, which, if successful, will be followed by an all-out commercialization program.

To achieve the program objectives, QNA applied and refined established industrial processes for the recovery of the required starting materials from biowastes and conducted a novel, epichlorohydrin-free VER synthesis. The overall process, illustrated in Figure 2, consisted of four distinct steps, each of which was evaluated in this program:

Step 1. Isolation of phenols from biowastes: Lignin separated from waste wood pulp by aqueous basic extraction was subjected to controlled pyrolysis in a supercritical-water reactor with no catalyst to produce phenol and 2-methoxy-phenol. These phenols can be separated from the reaction mix by extraction into water at high pH, leaving other undesirable byproducts in the reaction residue. The recovered phenols can be used directly for VER synthesis.

Step 2. Synthesis of bisphenol A (BPA) from the isolated phenols: The BPA was readily synthesized from phenol and acetone under acidic conditions.

Step 3. Synthesis of glycidyl methacrylate (GMA) from glycerin: Saponification of fats and oils during biodiesel manufacture produces glycerin as an unwanted byproduct. This glycerin

can be beneficially used to produce GMA for VER synthesis. This synthesis proceeds via chlorination of glycerin, followed by treatment with a base to yield glycidol. In this program, glycidol was reacted with methacrylic acid to produce glycidyl methacrylate directly while conversion of glycerin to glycidol was postponed to a follow-on program.

Step 4. Synthesis of VER monomer from BPA and GMA: This synthesis, which follows textbook chemistry, replaces toxic epichorohydrin with GMA derived from renewable sources. QNA evaluated the effectiveness of various approaches toward enhancing yields and reducing costs of this and the other synthesis steps in the process.

The recovery of glycerin from biodiesel wastes and the use of the resultant GMA for VER synthesis are both novel concepts not previously used commercially, but which will reduce the biowaste disposal problem and also enable an environmentally safe (non-epichlorohydrin) commercial process for VER synthesis.

3d. Phase I Technical Objectives

The key technical objectives are essentially to demonstrate that the four process steps described above constitute a suitable basis for the large-scale commercial production of VER. These objectives can be listed as follows:

- Demonstrate the production of phenol by supercritical water hydrolysis or dry pyrolysis of lignin under inert atmosphere.
- Demonstrate the synthesis of BPA from phenol and acetone
- Demonstrate the synthesis of GMA from glycerin
- Demonstrate the synthesis of VER from BPA and GMA
- Demonstrate that the synthesized VER meets key performance specifications

The chemical changes occurring in the four steps of the QNA process are illustrated in Figure 2.

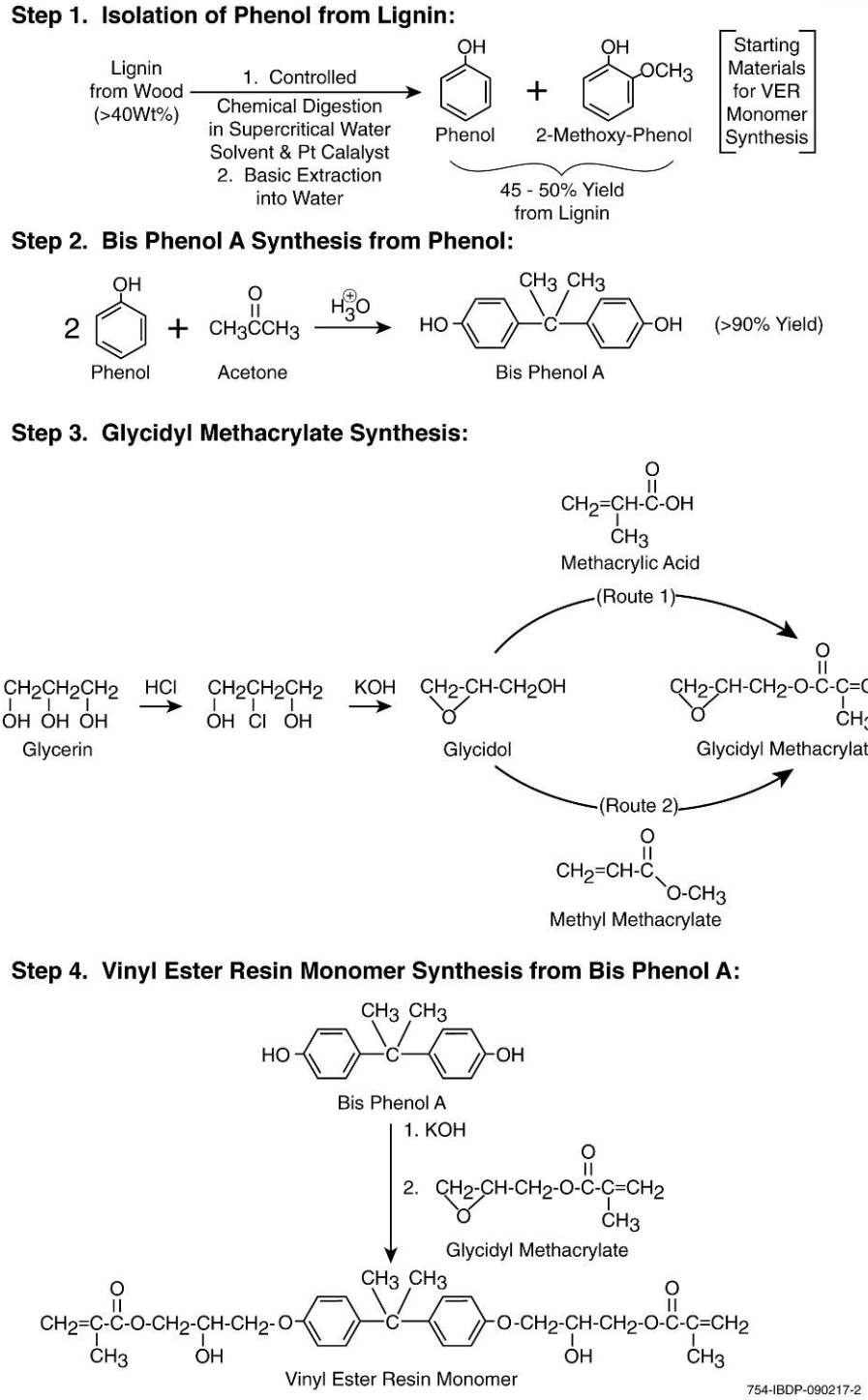


Figure 2 - QNA synthesis route to VER from lignin and glycerin renewable starting materials

Step 1. Phenol Production

Phenol is a valuable starting material for many organic chemicals including BPA used for synthesizing VER, epoxy and phenol-formaldehyde thermoset resins, as well as polycarbonate and polyacrylate thermoplastic resins. Annual production of phenol in the United States (Dow) exceeds 650 million pounds with virtually all of that being made using petroleum-based intermediates. Developing an alternate, inexpensive route to phenol from renewable natural products such as lignin will provide DoD with sustainable supplies of this valuable starting material without depleting food or petroleum reserves.

Prior to World War I, synthetic phenol was available and "natural" phenol was extracted from coal tar produced via controlled pyrolysis of bituminous coal in the absence of air. An entire industry was developed around the isolation of chemical products from coal tar but was abandoned when the price of petroleum fell to low values, making the synthetic approach economical. These early procedures can be successfully applied today to develop a renewable supply of chemical starting materials such as phenol, BPA and VER from lignin and glycerin natural products.

An attractive method for producing phenol from lignin is pyrolysis, but to enhance yields and suppress byproduct formation the pyrolysis conditions must be closely controlled. Pyrolysis in supercritical water offers a convenient means of providing the required degree of control for the following reason: at ambient conditions water has a dielectric constant of 78 and dissociates only slightly into hydrogen and hydroxyl ions. However, its dielectric constant is substantially lowered to 5-25 under supercritical conditions, a value approaching that of organic solvents. At these conditions, water is capable of dissolving organic compounds in its highly diffusive medium. In fact supercritical water acts like a strong catalyst whose activity can be adjusted simply by controlling the pressure and temperature in the supercritical range.

One example is of polymers like polyethylene terephthalate (PET). PET can be conveniently decomposed to their monomers when supercritical water is used as reaction solvent. The yield of terephthalic acid (TPA) approaches 100%, whereas the yield of ethylene glycol (EG) is merely about 30% at the same temperature.

Controlled pyrolysis of lignin in the absence of air in supercritical water (for example at 647K and 22MPa or 573K and 34.5MPa) produces significant quantities of phenol, methoxyphenol, dimethoxyphenol and methyl-substituted phenolic components that can be isolated and purified to provide a sustainable chemical feed stream of valuable starting materials. Reaction conditions such as temperature, pressure and time can be controlled to increase the yield of phenolic component to levels that exceed 40 percent. Other products are also formed during lignin pyrolysis under supercritical water reaction conditions that can be isolated and used as inexpensive fuel for heating the reaction process [1-13]. These products include combustible gases such as methane, mixtures of high heat content hydrocarbon oils and char/coke solid carbon residues. Figure 2 illustrates step 1 of the lignin pyrolysis reaction conducted in supercritical water solvent under high-pressure conditions.

Refinement and scaleup of the lignin pyrolysis process is expected to provide a sustainable, renewable source of phenol (convertible to bisphenol A) and other substituted phenolic compound. Such substituted compounds, methoxyphenol (guaicole), dimethoxyphenol (syringol), methylphenol(cresol) and catechol (dihydroxybenzene) can be valuable as low-cost intermediates for the organic synthesis industry.

Step 2. Production of BPA from waste-derived phenols

BPA is a key starting material for production of epoxy resins. As shown in Figure 2 step 2, it can be prepared by the acid-catalyzed coupling reaction of acetone with phenol. Hydrochloric acid (HCl) catalyses the condensation reaction at 90ºC producing BPA but with non-p,p' isomers. Nafion (perfluorinated resin sulphonic acid) is an alternative recyclable heterogeneous catalyst that is also highly efficient for the same condensation. However, milder Lewis acids such as Zeolite or acidic ion-exchange resins saturated with cystamine have been shown to catalyze the condensation with greater BPA selectivity and fewer side-reaction products [14-20].

Several catalysts and operating conditions were evaluated in the experimental investigation to determine the optimum procedure for BPA production.

Step 3. Production of GMA from waste-derived glycerin

An unwanted byproduct from saponification of natural fats and oils during biodiesel production, glycerin undergoes a range of reactions of industrial importance. For example, it can be used for the production of acrolein, widely used for organic synthesis and pharmaceutical manufacture, by catalytic gas-phase dehydration in presence of mineral acid. This reaction is an example of one that that may benefit by being carried out in supercritical water medium. In a reaction of more relevance, glycerin can be converted into glycidyl methacrylate, an intermediate required for VER synthesis. The process is carried out in three stages as shown in step 3 of Figure 2. First, dry glycerin is reacted with HCl gas in the absence of moisture to form glycerin monochlorohydrin (2-chloro-1, 3-dihydroxypropane) (II). Both anhydrous HCl and aqueous HCl can be used for this reaction. The glycerin monochlorohydrin then undergoes immediate ring closure (epoxide formation) upon treatment with base to produce glycidol (1, 2-epoxy-3-propanol) [III] as shown in Figure 3.

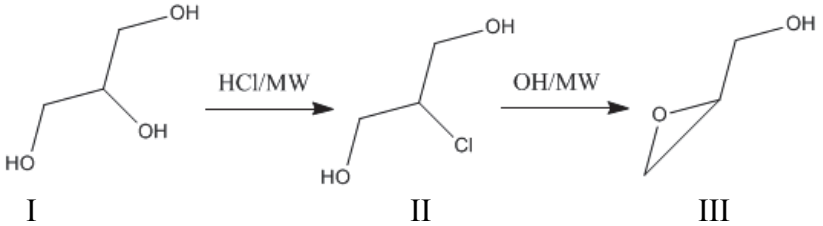
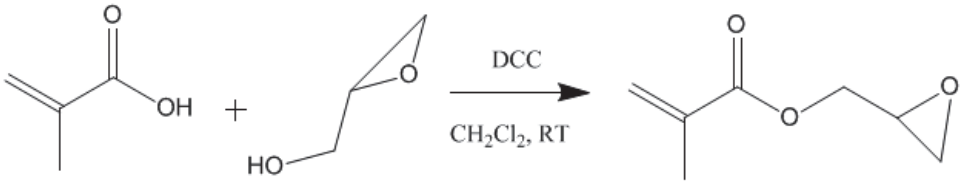


Figure 3 - Synthesis of glycidol (III) from glycerin (I)

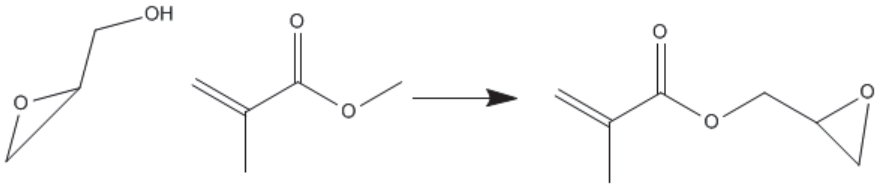
Finally, glycidol is converted to glycidyl methacrylate product. Two routes were investigated (see step 3 in Figure 2). Route 1 used a dicyclohexylcarbodiimide (DCC) coupling reaction of glycidol and methacrylic acid (MA) to make GMA at room temperature, as shown in figure 4.



VI III V

Figure 4 - Alternative route to GMA (V) by coupling methacrylic acid (VI) with glycidol (III) in DCC

Route 2 proceeded via ester interchange reaction with methyl methacrylate under basic conditions as shown in Figure 5. The reaction was driven to completion under mild conditions while methanol is distilled away. The overall yield of GMA from glycerin was greater than 85%. Both GMA synthesis routes were evaluated in the laboratory.



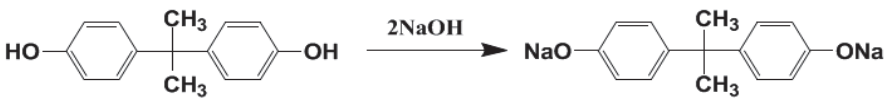
III IV V

Figure 5 - Synthesis of glycidyl methacrylate (V) via reaction of glycidol (III) with methyl methacrylate (IV)

Step 4. Synthesis of VER

Most commercial epoxy resins are currently prepared by the reaction of BPA and epichlorohydrin. Since epichlorohydrin is highly toxic it is not an acceptable starting material for the proposed environmentally compliant manufacturing process. To satisfy the environmental constraint, QNA proposed to replace epichlorohydrin in the VER synthesis reaction with GMA – step 4 in Figure 2. The direct reaction of BPA with GMA in the presence of benzyldimethylamine catalyst did not present any technical difficulties and proceeded in high yield to produce VER product.

In a second process that was attempted with a lower degree of success, the BPA produced in step 2 was not isolated, but was reacted in the same vessel with glycidyl methacrylate to produce the VER monomer [21]. The first stage, shown in Figure 6, was to convert the BPA into a soluble sodium salt by reaction with sodium hydroxide. As indicated in Figure 7, the soluble BPA then reacted in 1:1 ratio with the epoxide ring of the GMA. The vinyl ester monomer formed was filtered off with the aid of an organic solvent such as toluene. The toluene was subsequently removed by distillation under reduced pressure. The recovered monomer can be photo-polymerized by exposure to UV light or thermally cured in the presence of a peroxide catalyst to form the resins required to produce the desired composites.



VII VIII

Figure 6 - Conversion of BPA (VII) into a soluble sodium salt (VIII)

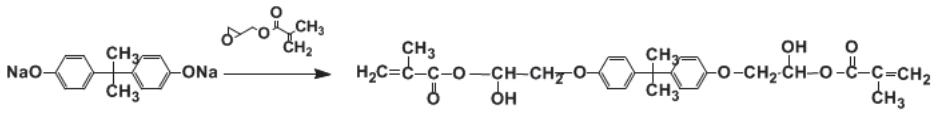


Figure 7 - Reaction of the soluble BPA salt (VIII) with GMA [V] to form VER monomer (IX)

3e. Specific Technical Challenges

Specific technical challenges that were encountered during completion of the Phase I program included the following:

- Isolation of phenol from the complex mixture of byproducts formed during supercritical water hydrolysis of lignin.
- Achieving each intermediate product derived from phenol in the yields reported in the literature.
- Establishing rigid safety procedures and protective equipment for conducting supercritical-water experiments at high pressure (4000psi) and temperature (400C).
- Applying safe handling procedures, clothing and equipment for phenol, BPA, VER and other potentially hazardous materials during laboratory experimentation.
- Establishing safety procedures for handling VER matrix resin during isolation, purification, analysis and storage.

3f. Risks involved

At the beginning of this SERDP limited-scope, proof-of-principle program, the risk of potential failure was high because of the complexity of the lignin reaction sequence and phenol conversion reactions. As the program progressed in an orderly fashion, however, we substantially reduced that risk by actually conducting the proposed lignin hydrolysis reaction and sequence of phenol transformation reactions leading to successful production of VER product. As a result of this effort, we believe that risk of successfully completing a follow-on program has been substantially reduced to acceptable levels.

3g. Innovative nature of the research

The innovation we proposed was to combine and apply literature reported reactions of lignin, glycerin, phenol, BPA and GMA to successfully produce VER in small quantities. Feasibility of our original concept for developing a sustainable, functional and economical vinyl ester resin for military composite weapon components from renewable resources was therefore successfully demonstrated.

3h. Scientific benefits from a successful proof of concept

The successfully demonstrated QNA approach offers the following potential benefits over petroleum-based VER composites:

- Elimination of dependence upon oil for manufacture of critical military and commercial composite components.
- Efficient use of lignin and glycerin, waste biomass byproducts, to produce high-value chemical products.
- Reduction of biomass waste and the associated disposal cost.

- Provision of economical, reliable sources of valuable chemical products including phenol, guaicol, syringol, catechol, acrylate monomers and polymers, carbon fiber, and clean-burning fuel gas, oil and carbon coke.
- Replacement of volatile, toxic, flammable styrene monomer in VER formulations with safer, nonvolatile methacrylate reactive diluents, thus providing better worker safety and environmental compliance.
- Development of potential sustainable routes to epoxy and phenolic composite matrix resins from bisphenol A produced using phenol derived from lignin.

4 Materials and Methods

4a. Materials

Lignin was purchased from Sigma-Aldrich (St. Louis MO) in two forms: basic and acidic. All chemical intermediates and starting materials used in chemical reactions were purchased from Aldrich. A high-pressure reactor was used for supercritical water hydrolysis reactions of lignin samples. Fourier-transform infrared spectra (FTIR), liquid chromatography / mass spectrometry (LC/MS), gas chromatography / mass spectrometry (GC/MS) and thin-layer chromatography (TLC) were the analysis methods used for product confirmation. TLC measurements were made using commercial TLC sheets coated with silica gel containing fluorosil fluorescent indicator for UV visualization of separated reaction components.

4b. Methods

The proposed QNA process was designed to produce vinyl ester resin (VER) from renewable lignin and glycerin starting materials by the sequence of synthesis reactions described in the preceding sections. The feasibility of the proposed process was to be demonstrated in a six-task experimental investigation shown in Figure 8 and described below. The four synthesis steps were carried out at laboratory-scale using conventional chemical equipment and reactors. All experimental work was conducted at QNA.

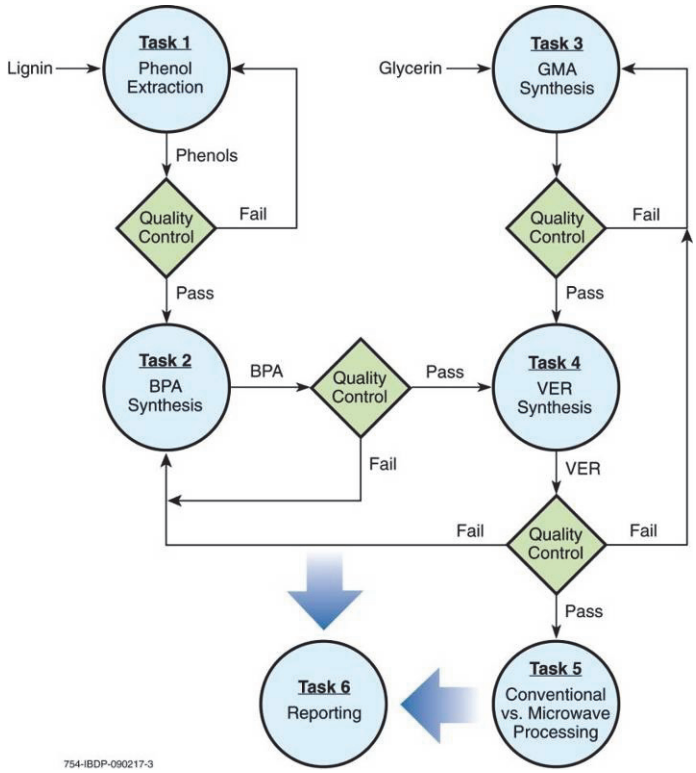


Figure 8 - Task flow

4c. Task 1 – Isolate Phenol and Methoxy-phenol from Lignin

Supercritical-water digestion and inert atmosphere pyrolysis techniques described in the literature [1-6] were used to convert purified lignin starting material into phenolic products. Considering the preferential degradation of the ether linkages of lignin, lignin was treated with supercritical water at 400C/ 4000psi pressure, and the resulting reaction mixture fractionated into three portions: the water-soluble, the methanol-soluble, and the methanol-insoluble fraction. Phenol was separated from other reaction products present in the digestion mixture by aqueous basic extraction. Phenolic extracts were acidified, re-extracted into solvent and then purified further by vacuum distillation. Sufficient phenol was collected during these experiments to provide an accurate assessment of chemical structure, actual yield obtained and anticipated yield following refinement of the lignin chemical digestion process.

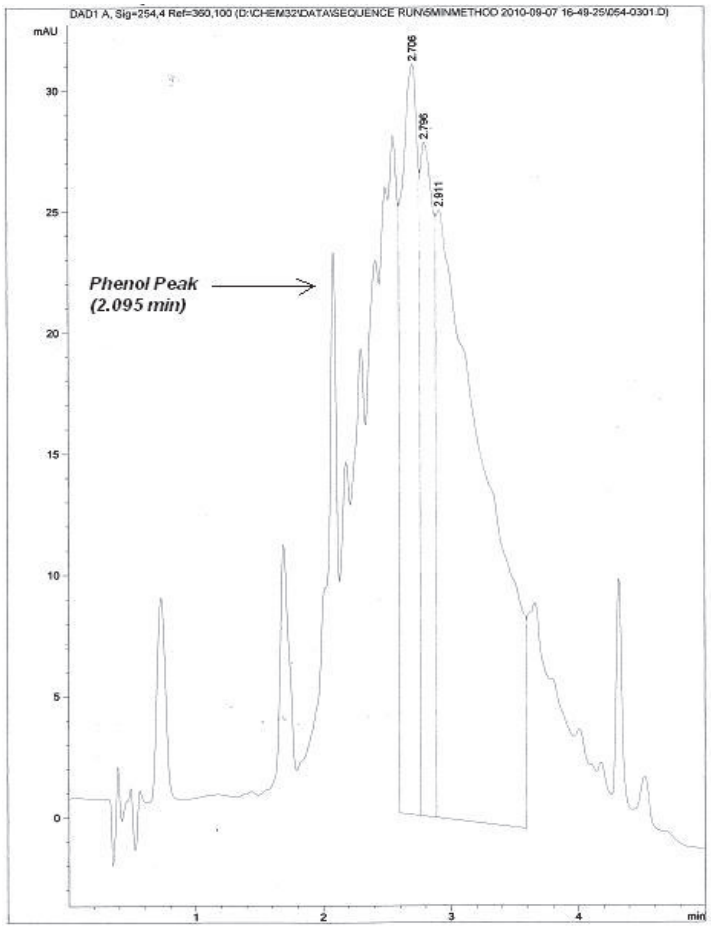


Figure 9: LC/MS trace of fractionated lignin hydrolysis product from supercritical water

The methanol-soluble fraction mostly comprising most of the lignin-derived phenolic products was analyzed by GPC and GC/MS to identify and determine phenol and its derivatives. Liquid pyrolytic products were examined qualitatively by GC-MS for the presence of phenols: phenol, o-cresol, guaiacol, catechol, 2, 4-dimethylphenol, 4-methylguaiacol and other phenol-based derivatives. Figure 9 shows an LC/MS trace of fractionated lignin hydrolysis product, demonstrating the presence of a phenol peak in the spectrum. Figures 14-21 are GC-

MS trace of a similar lignin hydrolysis product, showing peaks at mass values indicative of phenol and substituted phenolic products.

4d. Task 2 – Chemical Conversion of Phenol to Bisphenol A

This task was conducted at the multigram scale. An authentic sample of commercial phenol was reacted with acetone in the presence of mild Lewis acid catalyst to form BPA in yield greater than 90 %, as illustrated previously in Step 2 of Figure 2. The resulting BPA was precipitated and recrystallized from aqueous methanol, then further purified using high-performace liquid chromatorgraphy (HPLC). Purified BPA was characterized by melting point measurement, H-NMR, and FT-IR prior to use for synthesis of VER in Task 4. At least 10 grams of purified bisphenol A was produced in this task. Figure 10 (ignore mislabeling within the image) shows the NMR spectrum of purified bisphenol A synthesized from phenol.

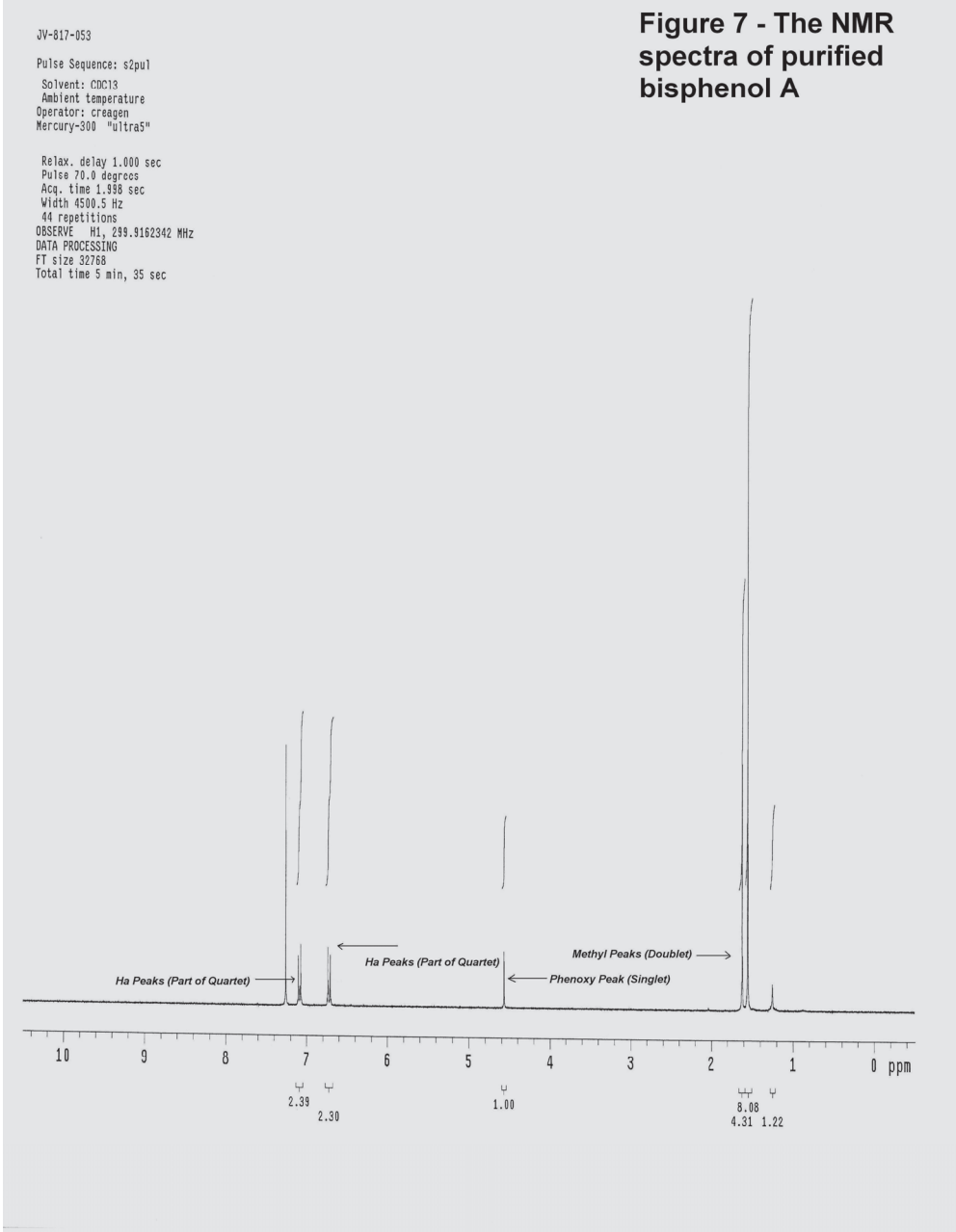


Figure 10 (ignore mislabeling in image): BPA NMR

4e. Task 3 – Synthesize Glycidol and GMA from Glycerin

In this task, glycerin was first to be reacted with dry HCl gas to produce glycerin monochlorohydrin, as illustrated previously in step 3 of Figure 2. This intermediate product would then be converted to glycidol by reaction with base, using a literature procedure [22]. A second method was explored which was a two step process to convert glycerin to glycidol. Glycerin was initially reacted with an anhydrous material under nitrogen to remove all water. It was then reacted with urea and zinc oxide to produce an intermediate; glycerin carbonate. The glycerin carbonate was then separated and reacted with calcium carbonate to produce glycidol. During Phase I, the synthesis of glycidol from glycerin was postponed for the

follow-on program in order to conserve valuable time and effort. Instead, a commercial sample of pure glycidol was reacted with methacrylic acid and dicyclohexylcarbodiimide (DCC) in dichloromethane solvent to produce GMA. An alternate route to glycidyl methacrylate that involved coupling of glycidol with methyl methacrylate under basic conditions to produce GMA via ester interchange was also evaluated as a more convenient, higher yield procedure to the desired product. At least 10 grams of purified GMA was produced. Figure 31 shows the NMR spectrum of GMA prepared in the same reaction.

4f. Task 4 – Synthesize and Characterize VER Monomer from Reaction of BPA with GMA

The procedure for reacting bisphenol A directly with glycidyl methacrylate in the presence of benzyldimethyl amine catalyst and no solvent was applied on the 50 gram scale in order to produce at least 10 grams of purified bisphenol A-glycidyl methacrylate (BIS-GMA), the chemical term for VER. The uncured VER monomer thus prepared was characterized using TLC, FTIR and NMR analysis. Figure 35 shows the FTIR spectrum of VER prepared by reaction of BPA with GMA in the presence of benzyldimethyl amine (BDMA) catalyst. Figure 34 shows the NMR spectrum of VER prepared in the same reaction.

5. Results and Discussion

5a. Task 1 – Pyrolysis of Lignin to Phenol in Supercritical Water Solvent

A high-pressure supercritical-water reactor was set up within the QNA laboratory. Supercritical water hydrolysis of lignin samples was conducted within the pressure reactor and reaction product was analyzed. Experimental details and the results are provided in the following paragraphs.

5a.1 Experiment

1. The high-pressure apparatus used was a HPI tubular batch reactor with internal capacity of 64mL, pressure rating to 20,000psi and temperature rating to 800F (427C). The tubular reactor was placed within a cylindrical, insulated heater tube equipped with heaters, thermocouple (outside the reactor) and controller. A ¼-inch-thick stainless steel plate was fastened in front of the reactor prior to each run for safety purposes to protect from potential rupture of the pressure vessel under heating and pressure conditions.
2. Lignin was purchased from Aldrich Chemical company in two forms: basic and organosolve.
3. Thin-layer chromatography (TLC) sheets contained silica gel with fluorescent indicator.
4. Silica gel for dry column chromatography was 250-mesh containing fluorescent indicator.
5. Chromatography column – a quartz column, 18” long x 0.5” in diameter was purchased from Finkenbeiner glass blowers, Waltham MA, and equipped with glass wool stopper to hold the dry column of silica gel used to conduct chromatographic purification of reaction product.

5a.2 Procedure

b.1.a Setup and testing of high-pressure reactor system

In support of task 1, we set up and modified a high-pressure systems (HPS) 64mL internal volume tubular reactor for use in lignin pyrolysis experiments using supercritical water at 400C/4000psi [1]. Figures 11, 12 and 13 illustrate the arrangement of the HPS system.

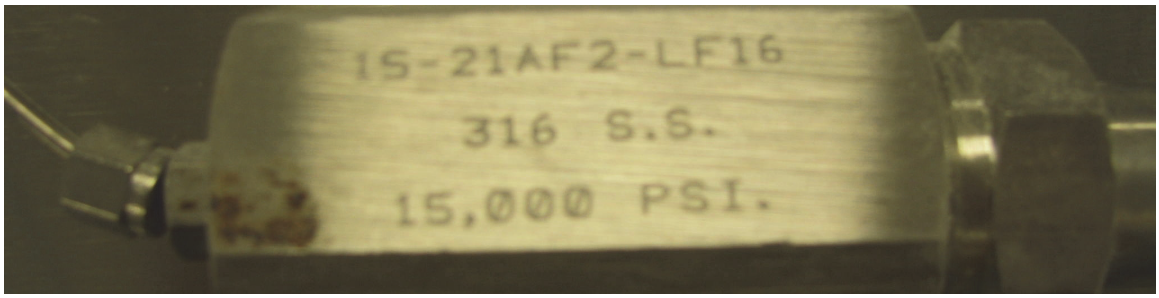


Figure 11 - HPS tubular pressure reactor system specifications

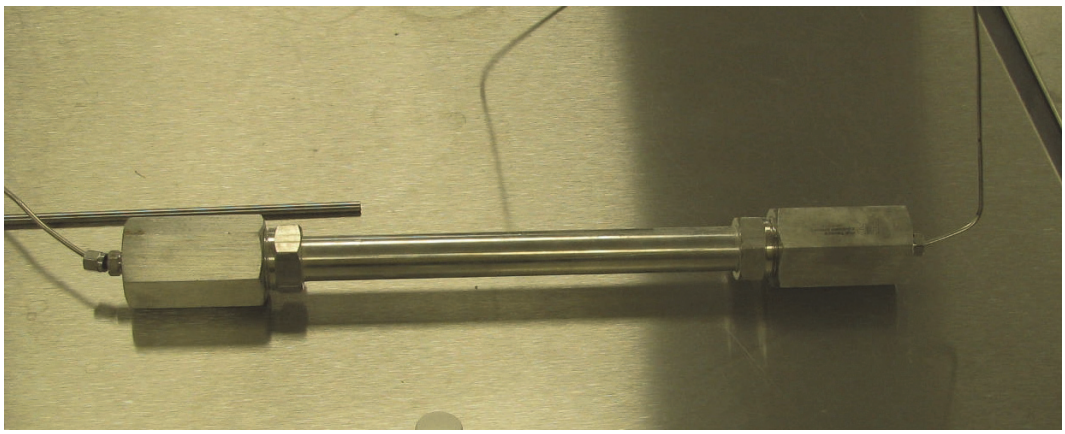


Figure 12 - HPS tubular pressure reactor system

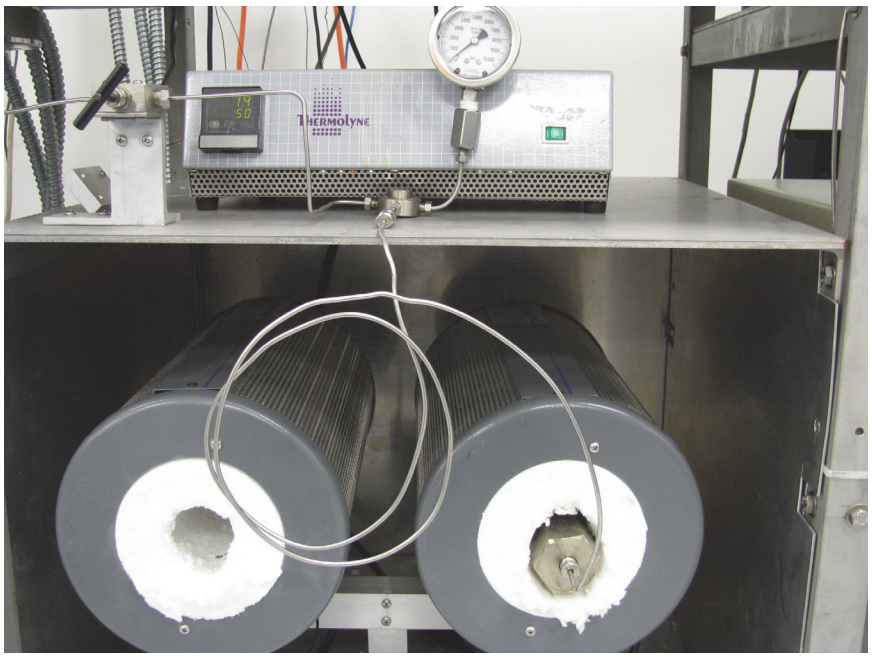


Figure 13 - HPS apparatus containing cylindrical heaters, pressure gauge and nitrogen tank for pressurization of starting lignin and water mixture

Literature references 1-3 provided critical information regarding the hydrolysis of lignin into phenol and substituted phenols in the presence of supercritical water only, with no catalyst added. Conditions that were reported in reference 1 to lead to isolation of phenol in substantial amounts were applied to our high-pressure reaction apparatus. The amount of water to add to the pressure reactor in order to develop 4000 psi pressure when the reactor was heated to 400C as calculated using steam tables.

b.1.b High-pressure reaction of basic lignin with water at 400C/4000psi pressure

Run 1: The cleaned, dried pressure reactor was pressurized to 1000psi nitrogen pressure and tested for leaks. No leaks were detected, indicating that the apparatus was ready for use. For run 1, 1 gram of basic lignin powder and 20 grams of water were added to the pressure reactor at room temperature. The reactor was closed tightly and pressurized with

1000psi nitrogen pressure prior to heating. The heater controller was then set to 400C and heating was initiated. Temperature in the vicinity of the pressure reactor was monitored continuously to make sure that target temperature was achieved without overshooting the set temperature and potentially developing higher pressure than desired. At a heater temperature reading of 425C the pressure gauge read only 2500psi and did not increase further. Reaction time was 4 hours of constant heating before heaters were turned off and the system allowed to cool to ambient temperature overnight. The cooled reaction vessel was opened with difficulty (future runs used "Never Seize" release agent on threaded joints prior to reactor closing).

b.1.c Procedure for workup of lignin pyrolysis reaction product.

The entire pressure vessel was rinsed out with acetone using a squirt bottle and combined rinses were evaporated. A dark tar was obtained (strong smoke odor) that was subjected to thin-layer chromatographic (TLC) analysis to determine the components present within the reaction mixture. TLC analysis (multiple elutions using hexane/ethyl acetate solvent mixtures) indicated that the reaction mixture isolated from run 1 contained a multitude of products, including one tentatively identified as *phenol, the desired product,* as indicated by its R_f value in comparison to the R_f value obtained for authentic phenol. Short-wavelength UV light was used to visualize the otherwise colorless spots on TLC, which appeared as dark shadows against a green fluorescent background. Authentic phenol was spotted alongside the run 1 reaction product showing a spot exhibiting an R_f identical with that attributed to the phenol component in the reaction mixture. TLC obtained for crude product isolated from Reaction 1showed a sizeable spot coinciding in R_f with the R_f value exhibited by an authentic phenol spot. Based upon these initial observations, plans were made to use dry column chromatography on the crude reaction product (tar residue) to separate the suspected phenol product from the reaction mixture and unequivocally identify that material as phenol using TLC, NMR, FTIR and GC/MS techniques.

b.1.d Procedure for dry column chromatography of crude lignin reaction product.

A solution of tar residue from run 1 in 5mL of acetone was added dry silica gel powder (column chromatography grade – 250mesh) until all of the solution was absorbed into the silica powder which was then air-dried to produce a free flowing powder containing crude reaction product. This powder was added to the top of a dry column of silica gel (0.5" diameter x 10" length) in preparation for preliminary cleanup of the reaction mixture. The column was eluted with a total amount of 100mL of methylene chloride, producing an initial band of product that eluted from the column and was collected in labeled beaker 1. After the methylene chloride elution had been completed, the column was eluted with higher polarity ethyl acetate solvent which stripped a second band from the column, leaving a dark residue at the top of the column. The second band, containing a major amount of product, was collected in labeled beaker 2 and the solvent from beakers 1 and 2 evaporated immediately on a rotary evaporator to make sure that sufficient product was isolated for unequivocal identification of the phenol component. An estimate of the yield from the reaction was made at that time; however, TLC analysis indicated the presence of the phenol component in run 1 about 2% (estimated by darkness intensity of product spot) and about 6% in run 2, which is described in a subsection that follows. Up to this time, however, the isolation of phenol component was only suspected from TLC

evidence, not proven by unequivocal means. Analysis of the reaction products using LC-MS and GC-MS, confirmed the presence of phenol in lignin hydrolysis residues.

b.2 Run 2 High-pressure reaction of basic lignin with water at 425C/5000psi pressure

Based upon the results from run 1, we modified the pressure reactor heating equipment to provide conditions that were much closer to the targeted values. In this reaction, heaters were set at 425C and the pressure was observed to increase to 5000psi where it was maintained for at least 4 hours before the heaters were turned off and the pressure reactor allowed to cool. In addition, a total of 5 grams of lignin was added to the reactor in order to provide larger amounts of product. Isolation of the crude reaction product from the pressure reactor in the usual manner produced a tar residue that indicated a much larger percentage of the phenol component than had been observed in run 1, the suspected reason being higher temperature and pressure conditions achieved during this reaction. The tar residue reaction product from run 2, after purification via dry column chromatography provided sufficient amounts of phenol product for characterization using TLC, LC/MS and GC/MS.

Unequivocal identification of phenol and substituted phenols as major products from lignin pyrolysis represented achievement of a major milestone in this program.

b.6 LC/MS analysis of crude lignin product from run 1

Figure 9, shown previously in section 4c, illustrated the results from LC/MS analysis of crude lignin reaction product before purification. The graph shows the presence of a strong peak in the region where phenol would be expected to appear superimposed upon additional overlapping peaks from closely related products; possibly, methoxyphenol, dimethoxyphenol, methylphenol and other lignin pyrolysis products reported previously in the literature [1-3]. Future lignin pyrolysis samples will first be purified using dry column chromatography prior to analysis using the LC/MS technique in order to greatly simplify the types and number of peaks obtained. As a result, the desired phenol peak should be more readily visible on the chart, providing additional spectral evidence of its presence. The results from LC/MS analysis of crude reaction product, although not unequivocal, provided strong evidence that phenol was present in substantial amounts, based upon peak size and position on the molecular weight scale of the MS detector

b.7 Redesign, assembly of high-pressure reactor system within a fume hood and testing.

In support of task 1, we modified and reassembled a HPS 64mL internal volume tubular reactor within a fume hood for greater safety and protection of personnel from fumes released during workup of pyrolysis reactions.

5a.3 Results

A series of 20 experimental reaction runs were conducted under varying conditions for the purpose of collecting sufficient crude phenol product for purification and unequivocal identification during this program. Table 1 lists the conditions and results for each run.

Table 1. Pyrolysis of Lignin to Phenol in Supercritical Water

Run	Date	Pressure (psi)	Temperature (C)	Water/Lignin Ratio (mL/gms)	Observed Results
1	8-28-10	1950	400	15.5/1	Pressure gauge line plugged
2	8-31-10	2800	425	20.5/1	Pressure gauge line plugged
3	9-2-10	3700	460	25/1	TLC showed high phenol content
4	9-15-10	4200	410	30/5	TLC showed high phenol content
5	10-19-10	4700	410	30/5	TLC showed high phenol content
6	10-21-10	5900	410	30/5	TLC showed high phenol content
7	11-1-10	4500	410	30/5	TLC showed high phenol content
8	11-2-10	6500	410	30/5	Overpressure due to line blockage
9	11-4-10	3800	400	30/5	TLC showed high phenol content
10	11-9-10	5700	400	305	Overpressure due to line blockage
11	11-10-10	3400	400	30/5	TLC showed high phenol content
12	11-16-10	5600	400	30/5	Overpressure due to line blockage
13	11-17-10	3100	390	25(1N NaOH/5	TLC showed low phenol content
14	11-23-10	3500	400	30/5	TLC showed high phenol content
15	11-30-10	3900	400	30/1	TLC showed high phenol content
16	12-2-10	3200	400	30(0.01N NaOH)/1	TLC showed low phenol content
17	12-7-10	3000	400	30/1	Pt foil added – no phenol detected
18	12-8-10	4600	400	30(0.01N NaOH)/1	Pt foil added – no phenol detected
19	12-9-10	1100	400	30/1	Pt foil added – no phenol detected
20	12-13-10	2500	400	30/1.2	TLC showed low phenol content

c.1. Thin-Layer Chromatographic Analysis of Products from Lignin Pyrolysis Experimental Test Matrix

TLC analysis of selected reaction products from runs No. 3-7, 9, 11, 13-15 indicated those conditions of pressure and temperature that had led to production of high phenol content products. These reaction products were combined and purified together via dry column chromatography to yield significant quantitities of pure phenolic product for unequivocal identification using FTIR, NMR and GC/MS analytical techniques. The average yield of phenol from the above series of lignin pyrolysis reactions was estimated by TLC to vary between 10-15 wt%. Based upon the results obtained thus far, we are confident that reaction conditions and work-up procedures can be adjusted to increase the yield of phenolic products to >25wt%. In addition, conversion of substituted phenolic byproducts to phenol via separate thermal treatment reported in the literature can potentially increase the yield of phenol from lignin to >45 %.

5a.4 Retrial

Pyrolysis Products from Supercritical-Water-Hydrolyzed Lignin

Pyrolysis using supercritical water was accomplished under gaseous nitrogen contained within a column roughly a foot in length and an inch in diameter. Five grams of alkali wood lignin (Sigma Aldrich) was combined with twenty five milliliters of double distilled water. Temperature was generally increased 100C every 20 minutes from ambient and adjusted according to the internal pressure of the column. It was noted that there was generally a lag time of 1hr to 45 min at 400C before the pressure began to increase to accommodate transformation of the wood lignin. Generally the column was heated for 4 hrs or more once the pressure had equilibrated and allowed to cool and return to ambient temperature overnight.

Once it was deemed safe the column was cracked and the product was removed using acetone. Both the char as well as the slurry which had gathered in the lines were removed, ground and refluxed for a 1.5 hrs and filtered in order to remove any residual product that might be in the char. The remaining product was roto-vaporated until a thick product was gathered.

A second means of pyrolysis was explored using a butane torch flame and glass trap. Similarly, the chamber was purged with nitrogen and 2-3 grams were heated to 500C until fully reacted. At the point in which heating began it was found that a 3 min delay before the lignin began to visibly expand and yellow gaseous smoke began to evolve. A good deal of the smoke gathered higher up in the chamber to form a brown resin which was then removed using acetone and filtered.

More-recent experiments indicate that it is possible to further separate this smoke by drawing a vacuum such that extraneous steps in refluxing and filtration may be eliminated or altogether eliminated. Furthermore, if a gaseous stage can be maintained, it might be possible to combine the production and separation steps.

Separation of Column Product
A quartz tube 45cm in length with a diameter of 3 cm was packed with silica gel 60, with fluorescent indicator 0.06-0.2 mm in particle size (Alfa Aesar) and plugged at either end with glass wool. Slurry of the product combined with silica gel was combined and then put into the head of the column. First the column was whetted and then elution using dichloromethane (DCM) and methanol (MeOH) was done in separate instances and monitored using UV-lamp.

Workup and Analysis
Trials were initially qualified according to TLC analysis and several products were selected for TGA and GC-MS analysis. TGA, using dynamic analysis, was also used as a preliminary selection before GC-MS to determine which products would not be feasible for GC-MS on account of difficulties in separation.

TGA was done using a TA instruments 2950 model using a ceramic internal oven and pans. Additionally, TGA of both the column char and torch char was done to determine if further extraction via refluxing was necessary, while samples of both 'raw products' was intended to determine the method requiring greater separation. Finally, analysis of the DCM and MeOH extracted product provided evidence as to which solvent would be preferable for separation.

GC-MS was done using a Shimadzu QP2010 equipped with a TD-20 thermal desorption unit and Supelco SPB-5ms plot (30mm x 0.25 x 0.25cm). Sample tubes were cleaned using an external desorption unit purged with nitrogen and then stuffed at either end with quartz wool. The products were rolled into a ball of quartz wool using acetone and then baked to remove excess solvent. The tubes were heated to 300C at the injection port held at 12 psi with a split ratio of 20:1 and temperature profile of 160-300C. Select samples were doped to identify the presence of phenol. Figure 14 shows GC/MS data for an authentic phenol sample. Figure 15 shows the GC/MS spectrum of column chromatographed char residue. Figure 16 shows the

GC/MS spectrum of flame-pyrolyzed lignin char residue. Figure 17 shows the GC/MS spectrum of raw lignin pyrolysis product. Figure 18 GC/MS spectrum of raw column product. Figure 19 GC/MS spectrum of methanol-extracted product. Figure 20 shows the GC/MS spectrum of dichloromethane-solvent-extracted product. Figure 21 shows the GC/MS spectrum of dichloromethane-solvent-extracted product doped with authentic phenol.

GC/MS data

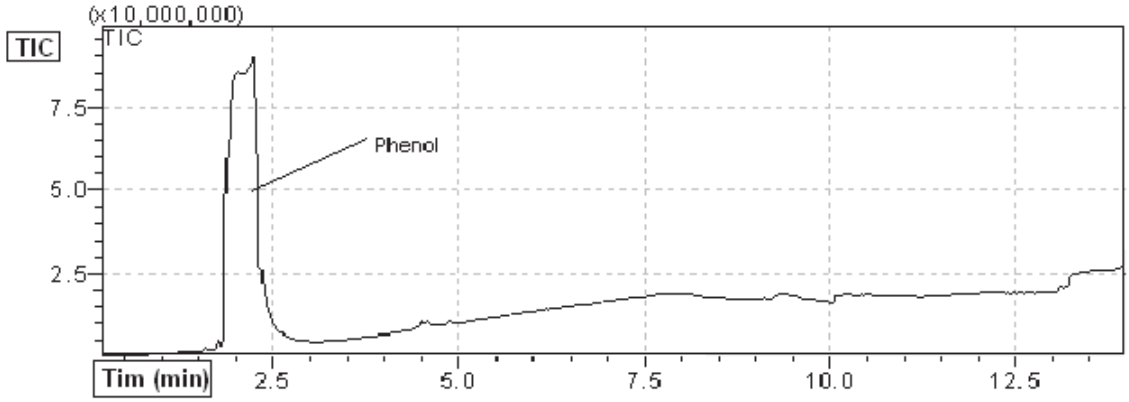


Figure 14 - GC/MS spectrum of authentic phenol

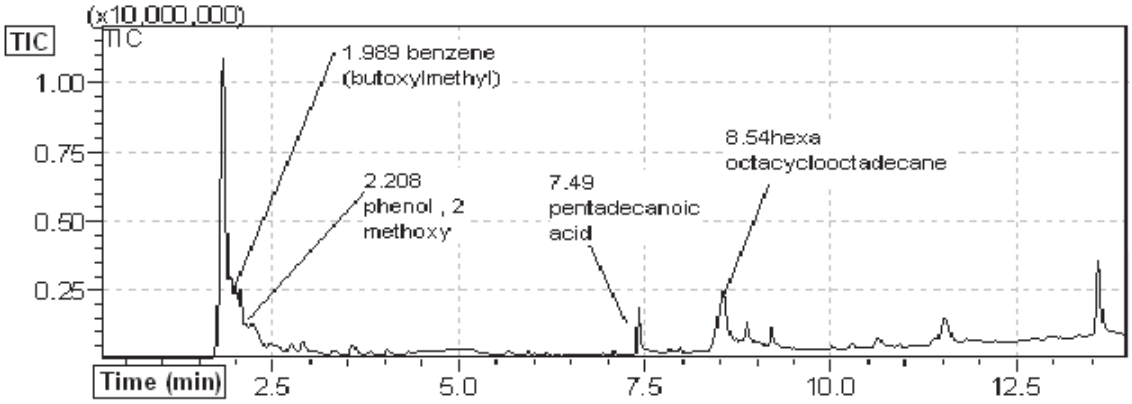


Figure 15 - GC/MS spectrum of column chromatographed char residue

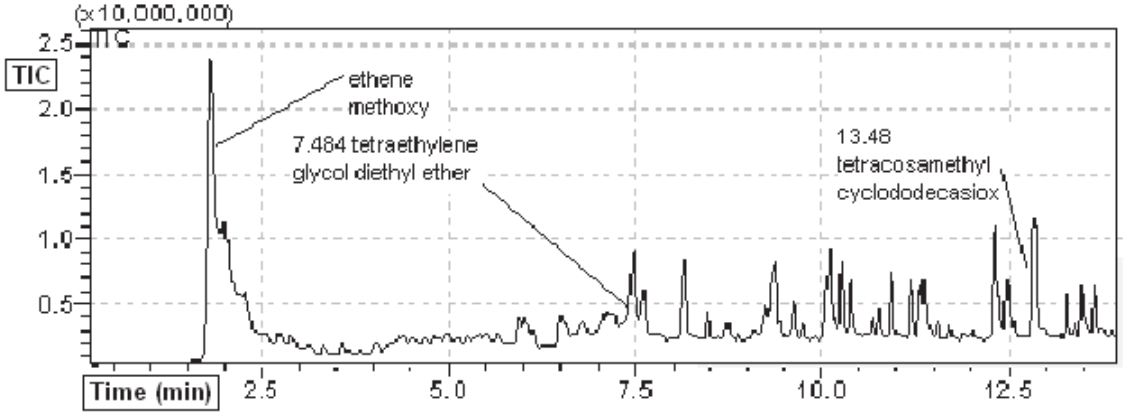


Figure 16 - GC/MS spectrum of flame-pyrolyzed lignin char

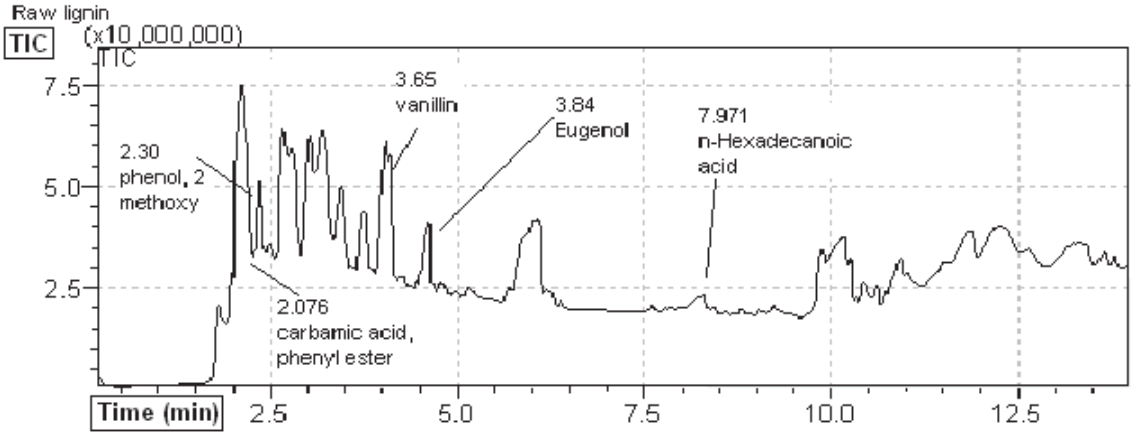


Figure 17 - GC/MS spectrum of raw lignin pyrolysis product

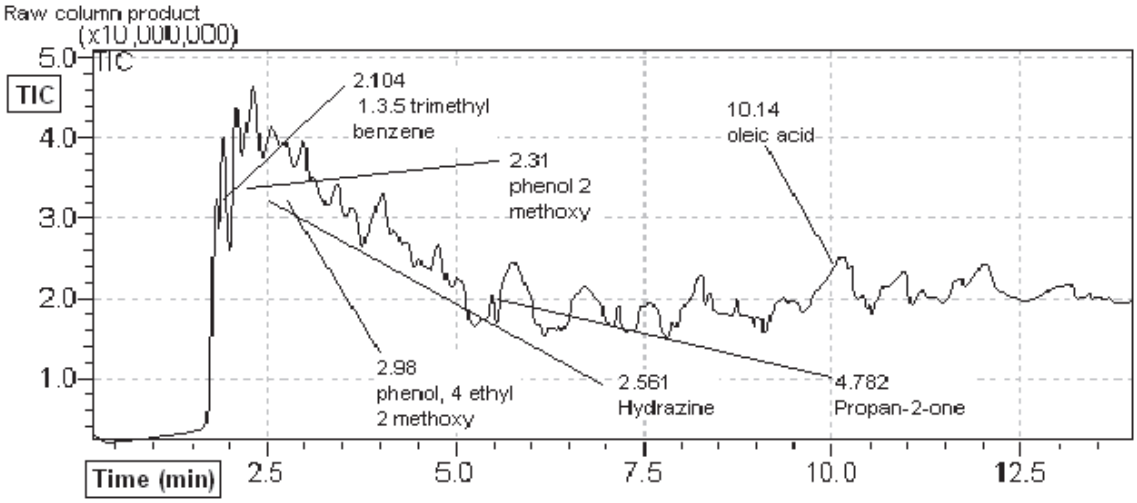


Figure 18 - GC/MS spectrum of raw column product

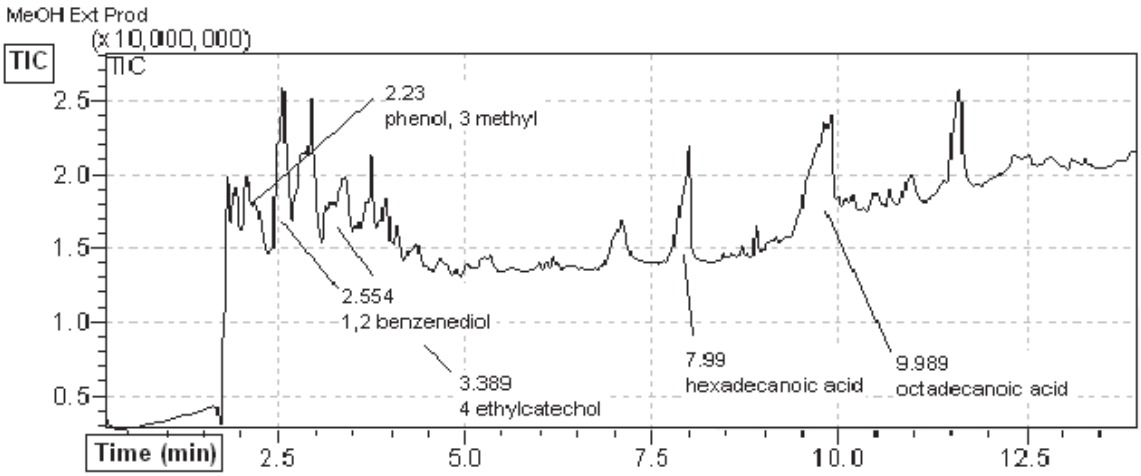


Figure 19 - GC/MS spectrum of methanol-extracted product

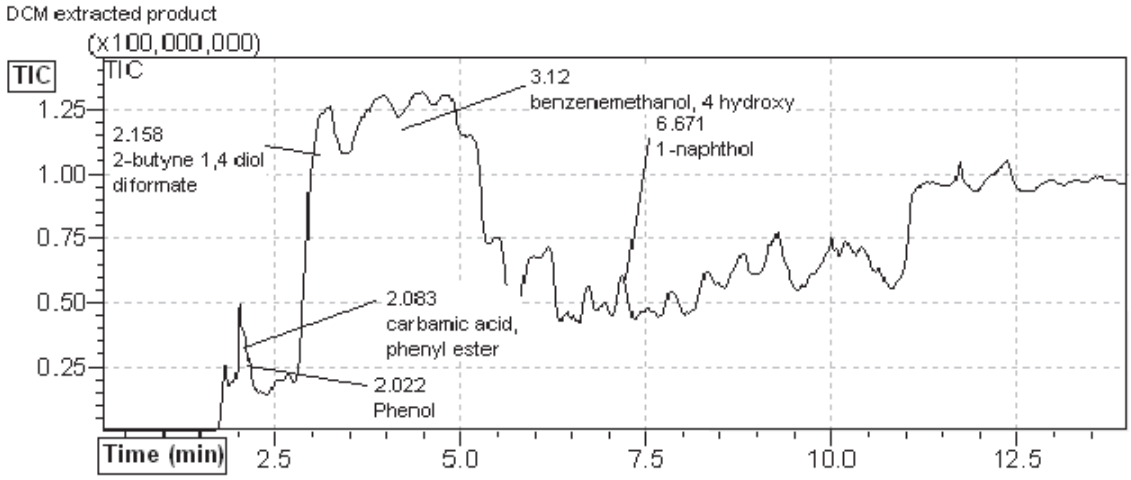


Figure 20 - GC/MS spectrum of dichloromethane-solvent-extracted product

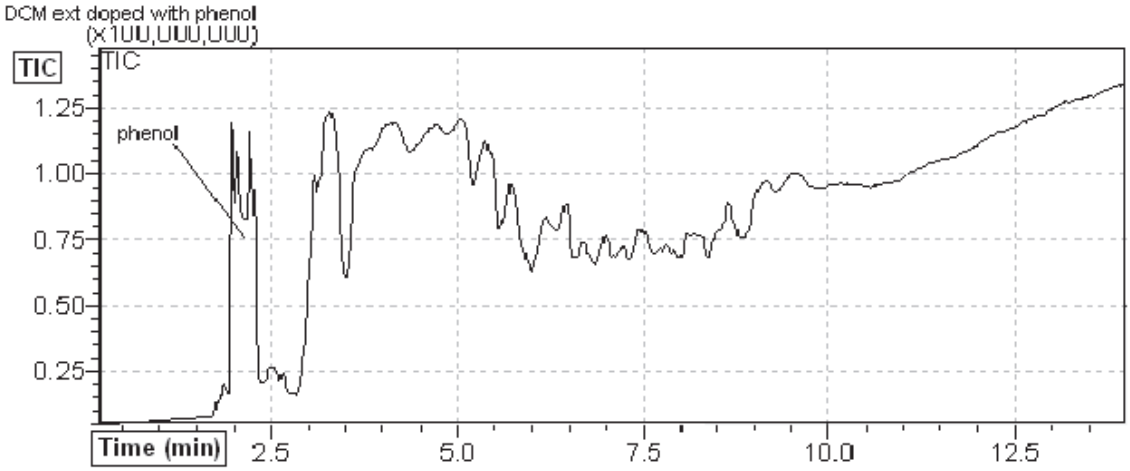


Figure 21 - GC/MS spectrum of dichloromethane-solvent-extracted product doped with authentic phenol

As can be seen by the above GC-MS readouts extraction of phenol may be better accomplished using dichloromethane. Combined solvent regimes of water, methanol and DCM might further enhanced the extraction in methods like reverse phase chromatography. Figure 22 shows the results from thermogravimetric analysis of lignin. Figure 23 shows the results from Thermogravimetric analysis of Raw product. Figure 24 shows the results from thermogravimetric analysis of char from column chromatography. Figure 25 shows the results from thermogravimetric analysis of flame-pyrolyzed lignin residue. Figure 26 shows the results from thermogravimetric analysis of methanol-extracted product. Figure 27 shows the results from thermogravimetric analysis of dichloromethane-solvent-extracted product.

Thermogravimetric Analysis

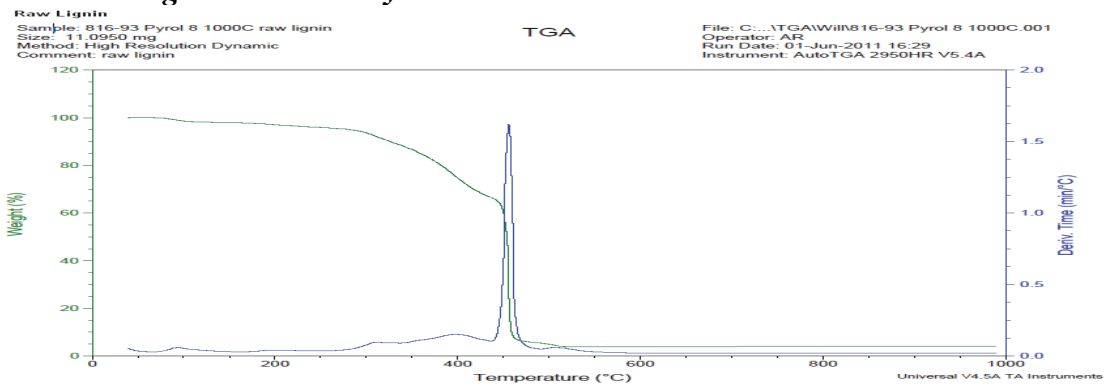


Figure 22 - Thermogravimetric analysis of lignin

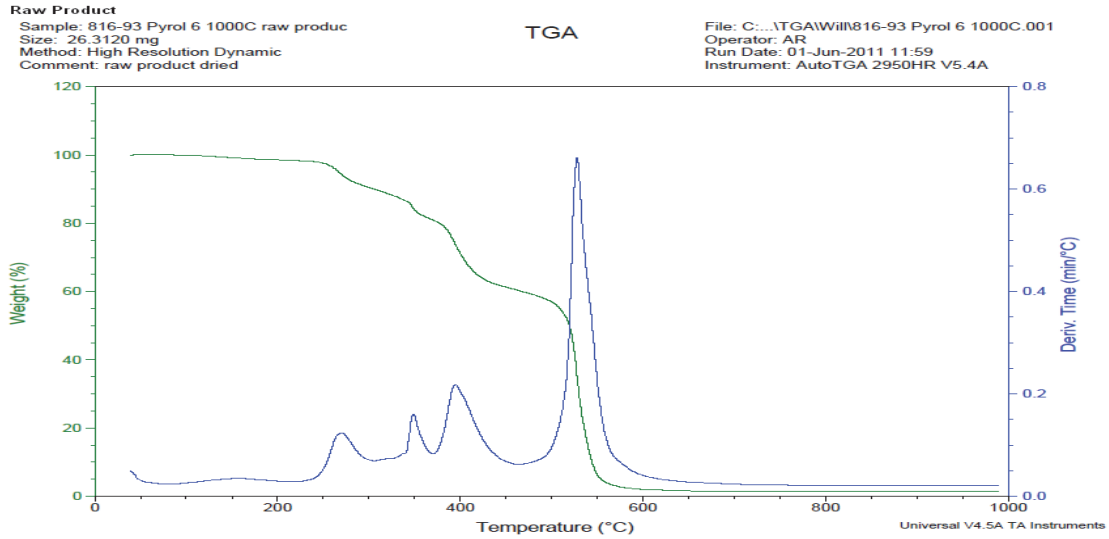


Figure 23 - Thermogravimetric analysis of raw product

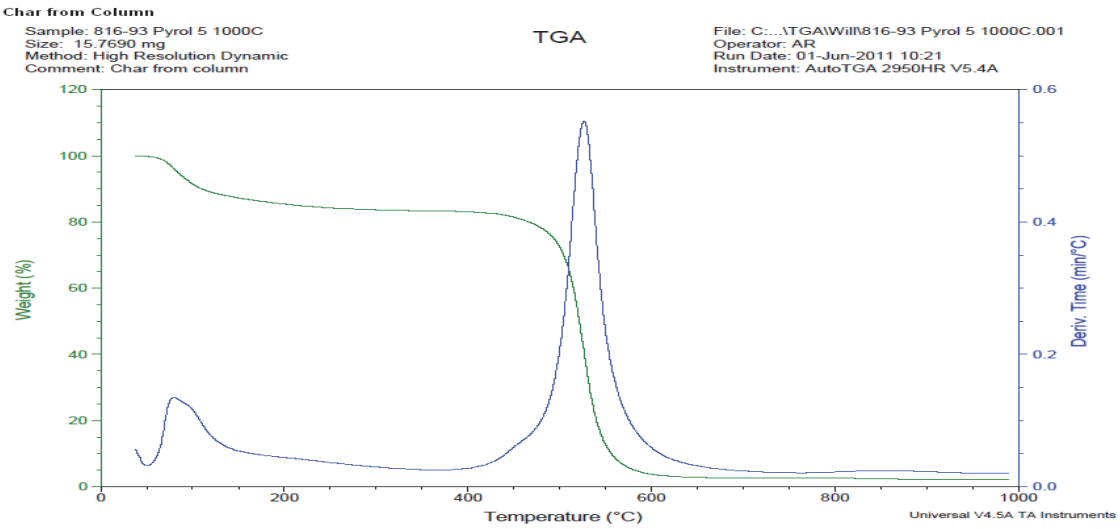


Figure 24 - Thermogravimetric analysis of char from column

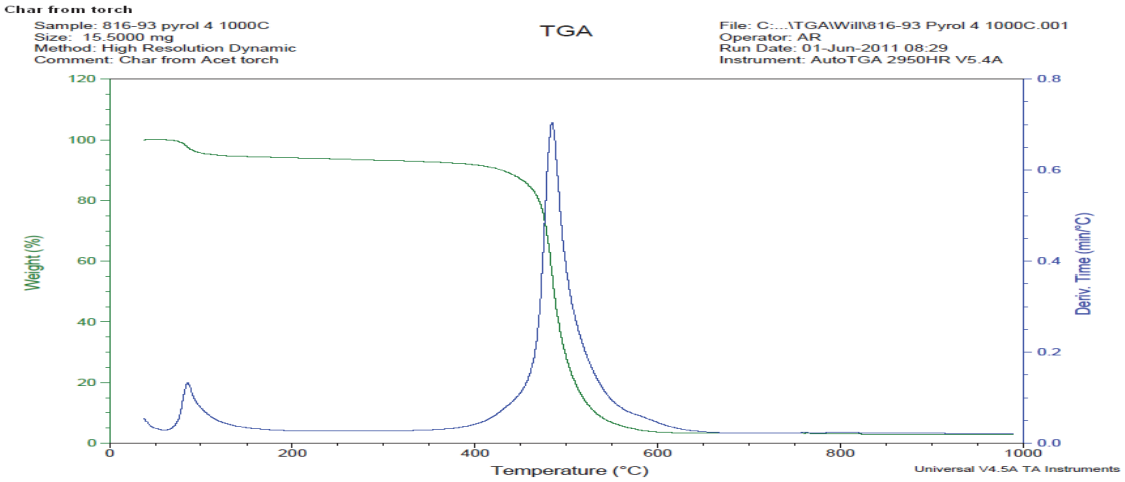


Figure 25 - Thermogravimetric analysis of flame-pyrolyzed lignin residue

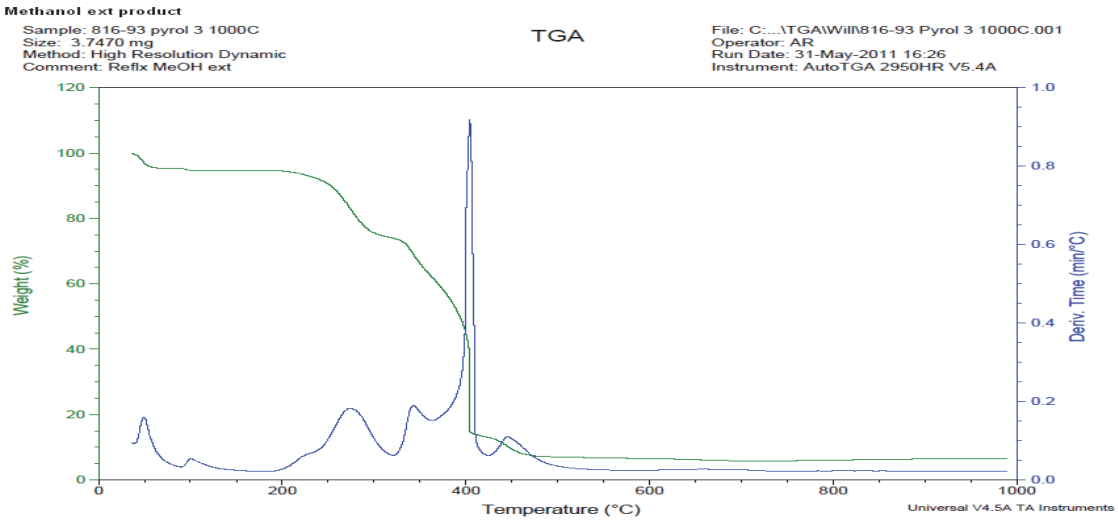


Figure 26 - Thermogravimetric analysis of methanol-extracted product

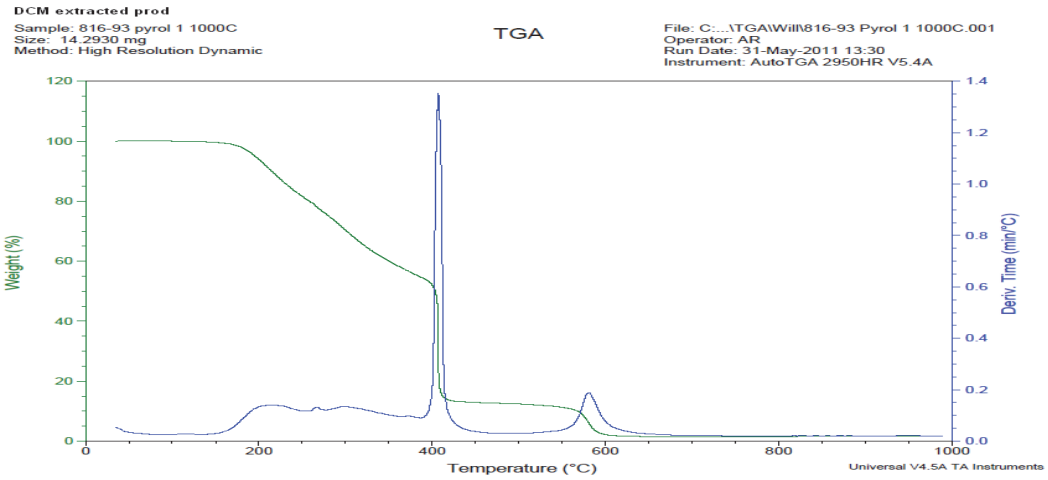


Figure 27 - Thermogravimetric analysis of dichloromethane-solvent-extracted product

Future Work

Despite the unique properties of supercritical water hydrolysis, it is still debatable whether the production of phenol under high pressure would be counteracted by le Chatlier's principle. Further exploration using flame pyrolysis methods with dry lignin powder at atmospheric pressure would be in order for both gaseous extraction and separation. Evidence from the flame pyrolysis studies suggests that the raw product from which phenol could be extracted gathers in the lines away from the char residue, as illustrated in Figure 28. Supercritical water may prove to be more useful in isolation than in production.

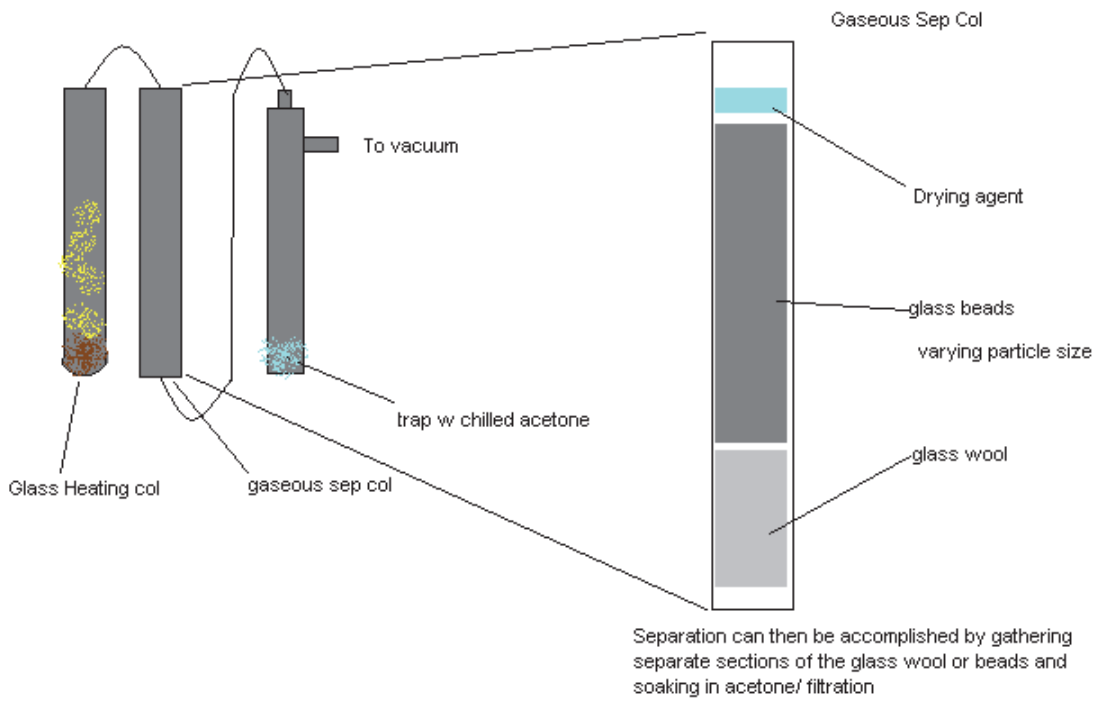


Figure 28 - A heated chamber for gaseous separation will likely be able to separate out the varying forms of products which evolve off and narrow down the phenol varieties we may encounter.

Furthermore, QNA has in its possession a Waters 2695 HPLC which if equipped with a new shutter in its 2995 PDA detector could provide far better chromatographic separation than the GC-MS methods and would be more cost-effective than sending out for LC-MS samples. Additionally, it could also be used as a secondary means of isolation beyond those mentioned above.

5b. Task 2 - Conversion of Phenol into Bisphenol A

The reaction yield of BPA was increased to about 89%, although the presence of residual unreacted phenol starting material was detected. BPA was purified to a high state of purity (>95%) by recrystallization from methanol solvent.

In support of task 2, we conducted a separate synthesis reaction, converting a commercial sample of phenol into bisphenol A. In this approach, no solvent was used and phenol was first melted then combined with acetone and HCl reactants in the presence of added thioglycolic acid catalyst. The mixture reacted immediately, providing crude product subsequently

identified as a mixture of bisphenol A and unreacted phenol. Figure 29 shows a picture of a thin-layer chromatogram of isolated bisphenol A showing the presence of unreacted phenol (high R_f spot) and bisphenol A product (lower R_f spot).

Experimental Procedure and Results

Phenol (94 g, 1 mol) was dissolved in acetone (12.75 g, .0219 mol) in a 500 mL three-neck round-bottom reaction flask equipped with cooling condenser. To the reaction flask, a catalytic amount of thioglycolic acid (0.5 g) was added, followed by slow addition of 33% hydrochloric acid (HCl) (12.75 g). The reaction was then allowed to stir at 60C overnight. The reaction product mixture was recovered from the reaction flask, then recrystalized in toluene to produce BPA (92 g, 40 %). The remainder of the phenol can be recycled for its subsequent BPA synthesis.

1. Commercial Phenol
2. Crude Product
3. Commercial BPA
4. Purified Product

Figure 29 - Reproduction of Thin-Layer Chromatogram for BPA Synthesis Reaction

Milestone: Demonstrate Synthesis of Bisphenol A from Phenol

Bisphenol A was successfully produced in >90% yield by reaction of a commercial sample of phenol, under acidic conditions and in the presence of a catalyst. The crude product mixture was analyzed by LC/MS analysis which showed the parent ion peak for bisphenol A in the reaction product. Unreacted phenol was also detected in the product as an impurity, present in substantial amounts. TLC analysis confirmed the presence of phenol impurity in bisphenol A product. R_f values for authentic bisphenol A and authentic phenol samples were identical with R_f values obtained for synthesized bisphenol A product and phenol impurity, respectively. Experiments were conducted during the fourth Quarter to purify bisphenol A product from traces of phenol contaminant via recrystallization. Successful achievement of >95% BPA purity was demonstrated by TLC and NMR analysis of recrystallized material.

5c. Task 3 – Synthesis of GMA from Glycidol

Two different literature procedures were investigated to synthesize GMA from glycidol [24, 25]. The first reacted glycidol (1,2-epoxy-3-hydroxypropane) with methacrylic acid in the presence of dicyclohexylcarbodiimide (DCC) dehydrating agent and methylene chloride solvent. Glycidol (5 g, 0.068 mol) / methacrylic acid (5.81 g, 0.068 mol) / dicyclohexylcarbodiimide (16.8 g, 0.081 mol) / dichloromethane (100 mL) were combined within a stirred glass reaction flask for 3 hours. The solution became cloudy throughout the reaction time

period and appeared as a semihomogenous liquid with particulates floating about, indicating possible presence of the DCC urea reaction product with water (insoluble solid).This liquid was collected and analyzed via TLC and NMR analysis alongside both of the reactants used.

The second method reacted glycidol with methyl methacrylate in the presence of 2, 4-dimethyl-6-tert.butyl phenol and potassium cyanide [24]. The mixture was heated between 70C and 80C for two hours, with the product being distilled off. TLC and NMR analysis verified the presence of the GMA. Figure 30 shows the NMR spectrum of glycidol synthesized from glycerin, while Figure 31 shows the NMR spectrum of synthesized GMA product.

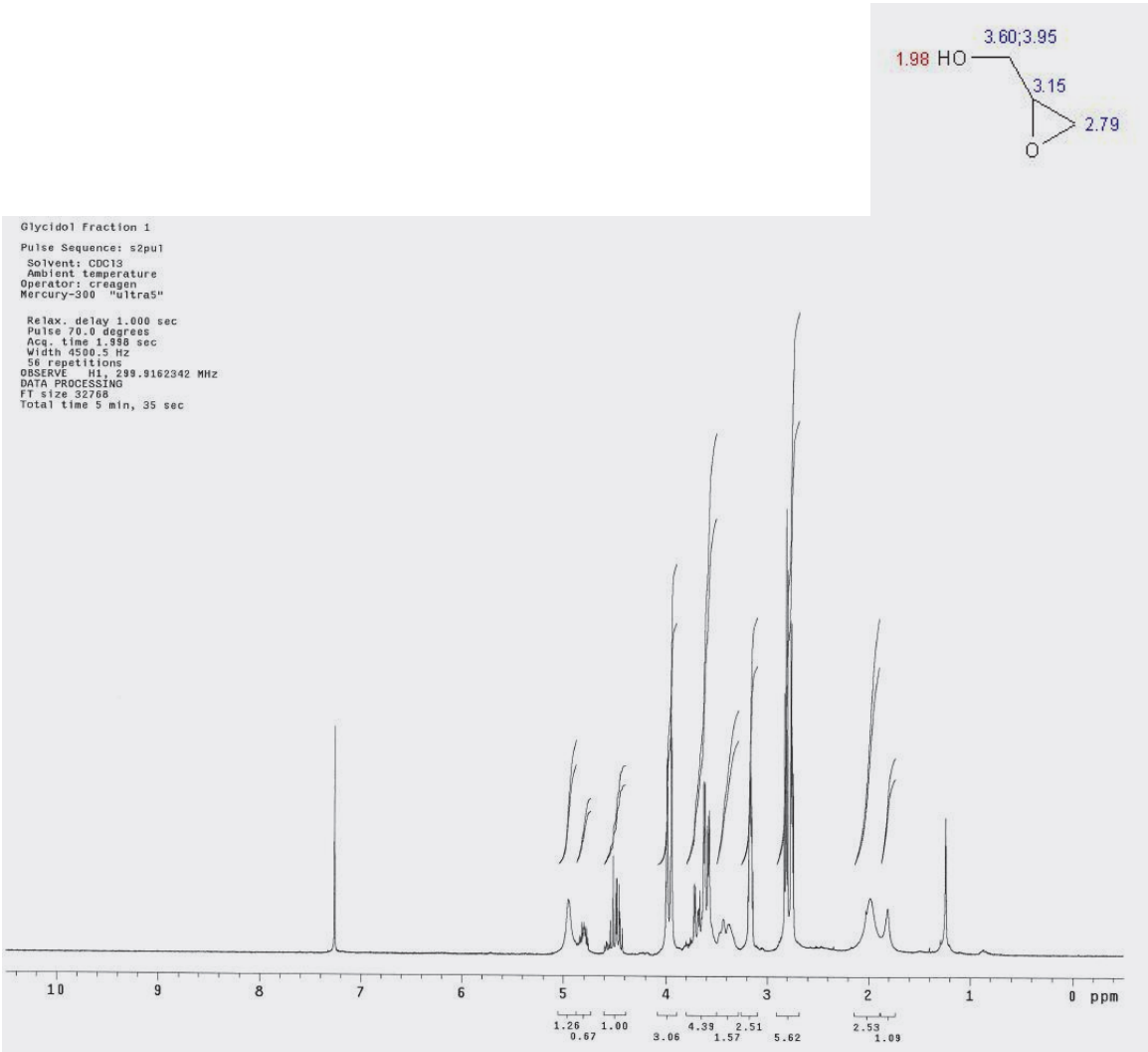


Figure 30 - NMR spectrum of glycidol synthesis product method
Peak positions: ^{1}H NMR (in $CDCl_3$) δ 1.98 (1H, br), 2.79 (2H, m), 3.15 (1H, m), 3.60 (1H, dd, *J*=4.5Hz, *J'*=12.6Hz), 3.95 (1H, dd, *J*=2.1Hz, *J'*=4.8Hz)

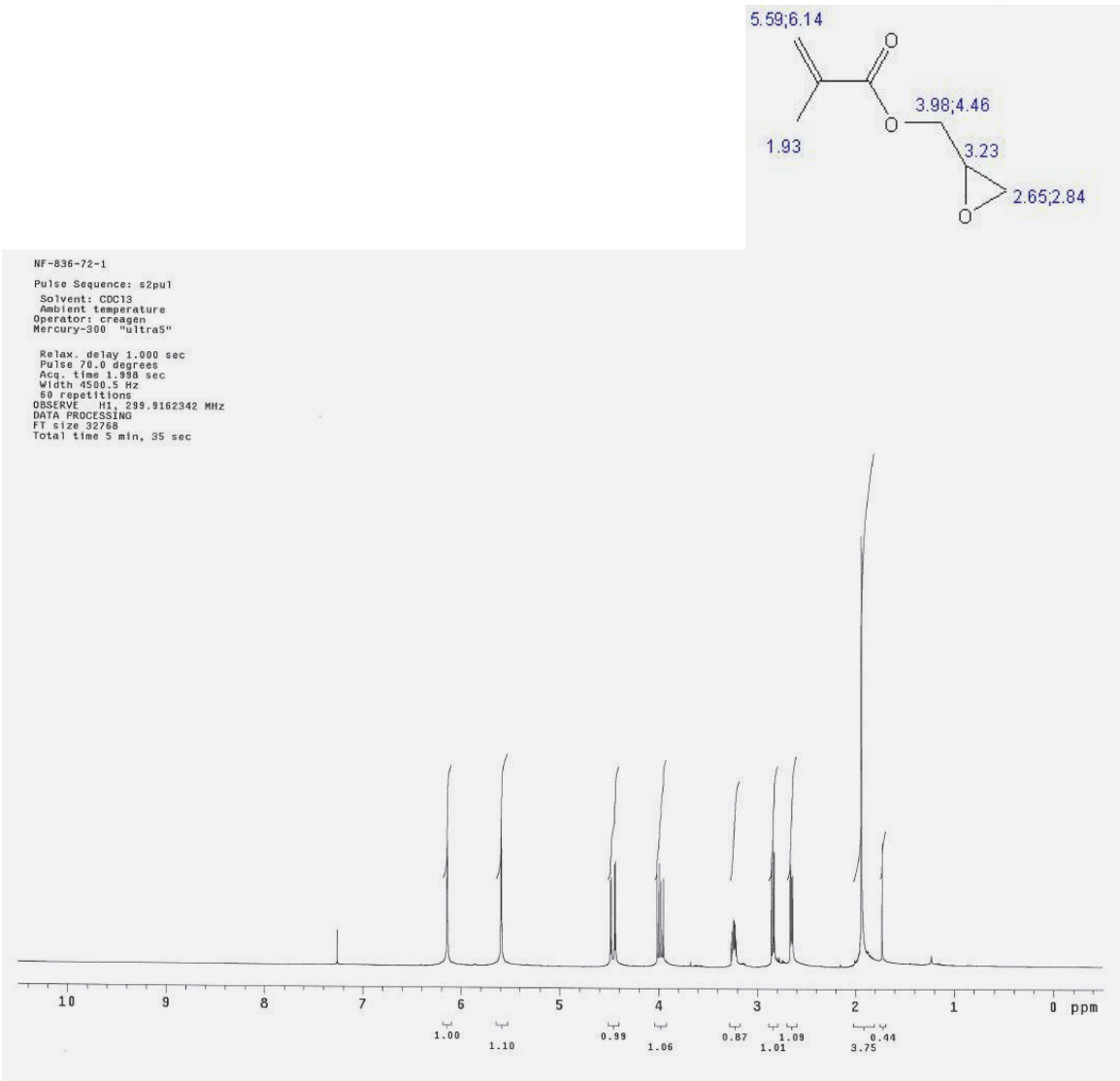


Figure 31 - NMR spectrum of synthesized GMA product
Peak positions: ^{1}H NMR (in $CDCl_3$) δ 1.93 (3H, s), 2.65 (1H, , dd, *J*=3.0Hz, *J'*=4.8Hz), 2.84 (1H, dd, *J*=4.2Hz, *J'*=5.1Hz), 3.23 (1H, m), 3.98 (1H, dd, *J*=6.3Hz, *J'*=12.3Hz), 4.46 (1H, dd, *J*=3.0Hz, *J'*=12.3Hz), 5.59 (1H, m), 6.14 (1H, m)

Synthesis of Glycidol from Glycerin

A synthesis from the literature was selected to convert natural biowaste, glycerin, into GMA, an important reactant required for VER synthesis [22]. In this route to GMA from natural products, glycerin is first reacted with HCl to produce the chlorohydrin intermediate 2-chloro-1,3-dihydroxypropane which, upon treatment in-situ with base, undergoes chloride ion elimination and ring closure to produce glycidol (1,2-epoxy-3-hydroxypropane) in high yield. Following purification via distillation in the presence of hydroquinone inhibitor, glycidol is then further reacted with methacrylic acid to produce GMA.

Another path using glycerin was explored towards the end of the project. In the second procedure glycerin was placed under nitrogen in the presence of magnesium sulfate anhydrous

for an hour to remove all water [25]. Urea and zinc oxide were then added and reacted for a minimum of six hours. The product was filtered and further reacted with calcium carbonate. The product was distilled and analyzed for the presence of the expected compound using TLC (Figure 32).

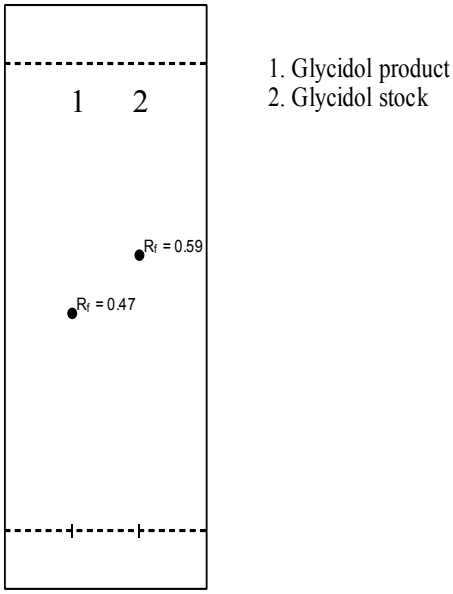


Figure 32 - Reproduction of thin-layer chromatogram for glycidol synthesis reaction

During this project, we successfully demonstrated the production of GMA using both methods of synthesis. The first step in that synthesis, namely, conversion of glycerin to glycidol via consecutive reaction with urea, zinc oxide and calcium carbonate, respectively, was reserved for further procedural improvement during the follow-on program to conserve valuable time and funding.

Milestone: GMA Synthesized from Glycerin. Feasibility of synthesizing glycidyl methacrylate via two different reaction methods was successfully demonstrated. The first reacted glycidol with methacrylic acid in the presence of DCC and the second reacted glycidol with methyl methacrylate in the presence of potassium cyanide and 2, 4-dimethyl-6-tert.butyl phenol. Initial GMA product obtained contained impurities which were removed by flash chromatography. Refinement of the synthesis of glycidol from glycerin will also be conducted during the program.

5d. Task 4 – Synthesis and Characterization of VER from BPA and GMA

- Synthesis of VER monomer via reaction of BPA with sodium hydride in dimethylformamide (DMF) solvent followed by reaction of the resulting bis-sodium phenoxide salt of bisphenol A with glycidyl methacrylate was conducted. Analysis of reaction products using LC/MS, NMR and FTIR indicated that VER monomer had been successfully produced. However, further purification of the reaction mixture was required to produce sizeable quantities of VER monomer that was

free from polymerized byproducts and suitable for unequivocal identification using spectral characterization methods.

- An alternate approach to VER monomer via direct reaction of BPA with GMA in the presence of benzyldimethyl amine catalyst and no solvent was successfully completed.

Purified bisphenol A (BPA) prepared during Task 2 from phenol was employed to further synthesize VER monomer in a straightforward manner, using the direct reaction approach.

5d.1 Materials

Sodium hydride (96% pure), anhydrous N, N'-dimethyl formamide (DMF), GMA (CAS: 106-91-2), BPA (CAS: 80-05-7). All the chemicals were procured from Sigma-Aldrich (St. Louis MO) unless stated otherwise.

5d.2 Method 1

Sodium hydride (564 mg, 23.5 mmol) was added under a flow of nitrogen to the 500 mL size three neck round bottomed flask equipped with a cooling condenser. Anhydrous DMF (150 mL) was added through a funnel to make NaOH slurry. The reaction vessel was cooled to 0C by placing it in an ice-salt bath. When the reaction mixture cooled to 4 C, BPA (2.5 g, 10.95 mmol) was dissolved in DMF and added to the reaction mixture. The addition of GMA (3.2 g, 22.47 mmol) was added dropwise to the reaction mixture. The reaction temperature was raised to room temperature by removing the cooling bath. After 1 hr the reaction T was further raised to 50C and maintained overnight.

5d.3 Workup

A 5 mL aliquot of water (5 g, 0.277 mmol) was slowly added to the reaction mixture to scavenge the remaining NaH if any was unreacted. The solution mixture was poured over ice water, followed by extraction using dichloromethane twice (2 x 100 mL). The organic layer was isolated and washed with water. The mixture was dried with brine solution, followed by drying over anhydrous magnesium sulfate. The filtered organic fraction was concentrated on a Rotovap to remove dichloromethane and then under high vacuum to remove DMF. The resulting GMA was 2.4 g (25 %).

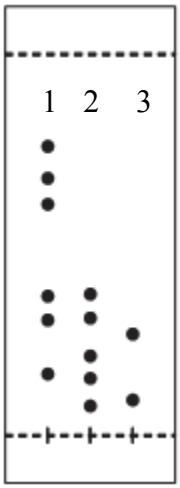
5d.4 Characterization

VER monomer isolated from the above synthetic reaction procedure was analyzed using LC-MS, NMR and FT-IR techniques. Spectroscopic analysis showed that VER monomer was present in the product although significant amounts of polymer had formed during the reaction and residual starting materials were still present.

5d.5 Method 2: No Solvent

BPA (1.25g , 0.055 mol) and catalytic BDMA (1.5 g) were dissolved in 20 mL DMAc and then added to the reaction vessel at 60C and stirred. GMA (2.4 g, 0.0168 mol) was later added to the vessel. The reaction was stirred overnight.

The reaction product mixture was collected in ether, DCM, and MeOH. Figure 33 shows a reproduction of thin-layer chromatogram of VER product.



1. Ether Sol.
2. DCM Sol.
3. MeOH Sol.

Figure 33 - Reproduction of Thin-Layer Chromatogram of Product

5d.6 Synthesize and characterize vinyl ester resin (VER) monomer directly from BPA and GMA and no solvent

Attention was directed toward synthesis of VER monomer via direct reaction of GMA with BPA in the presence of benzyldimethylamine catalyst and no solvent. Application of this method produced VER monomer in high yield (>90%) and purity. Figure 34 shows the NMR spectrum of VER monomer, Figure 35 the FTIR spectrum of purified VER monomer, and Figure 36 the LC/MS data acquired for VER monomer.

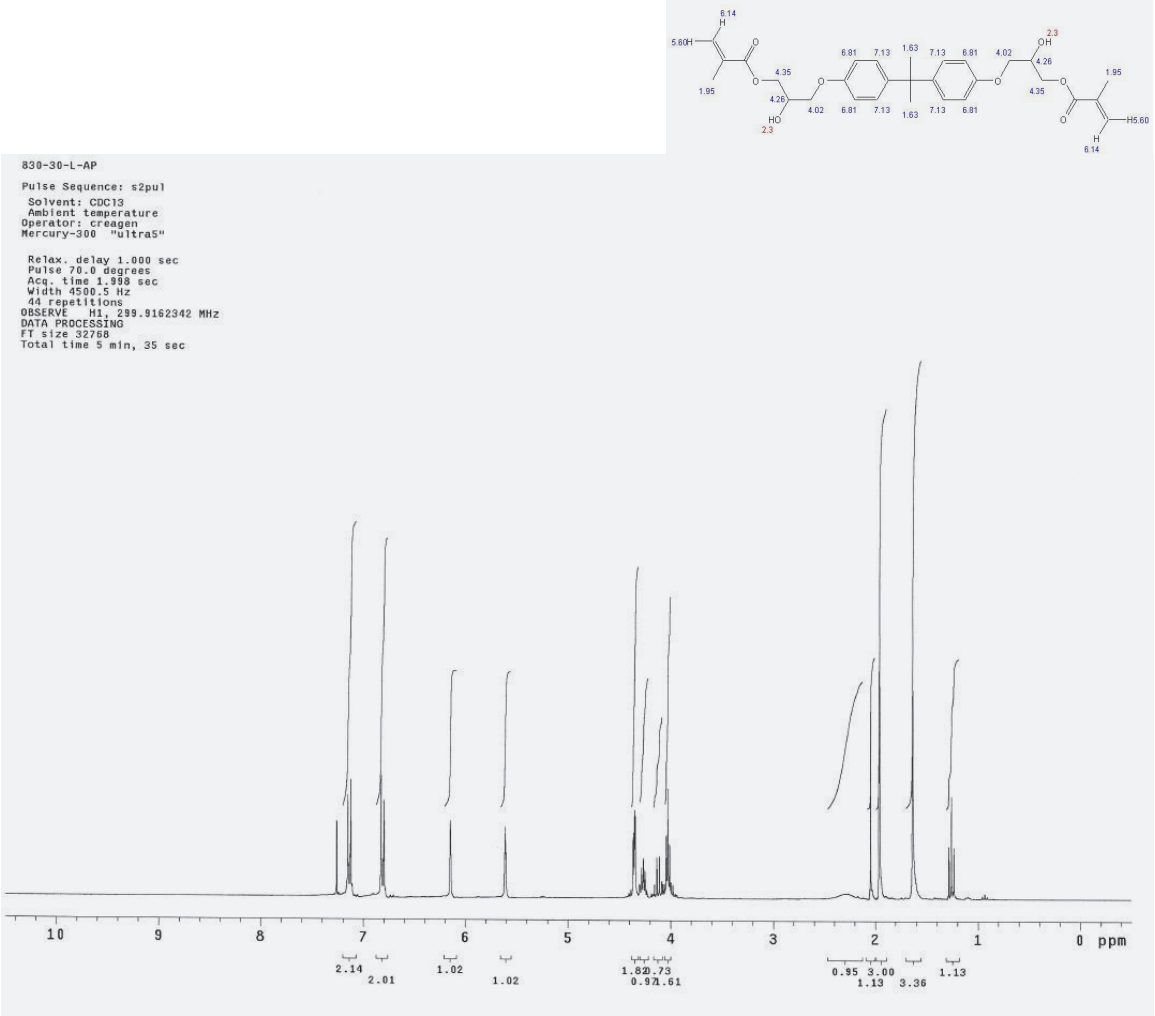


Figure 34 - NMR spectrum of VER monomer
Peak positions: ^{1}H NMR (in $CDCl_3$) δ 1.63 (3H, s), 1.95 (3H, s), 2.30 (1H, br), 4.02 (2H, t, *J*=4.5Hz), 4.26 (1H, t, *J*=5.1Hz), 4.35 (2H, dd, *J*=1.8Hz, *J'*=4.8Hz), 5.60 (1H, s), 6.14 (1H, s), 6.81 (2H, dd, *J*=1.2Hz, *J'*=6.6Hz), 7.13 (2H, dd, *J*=1.5Hz, *J'*=6.9Hz)

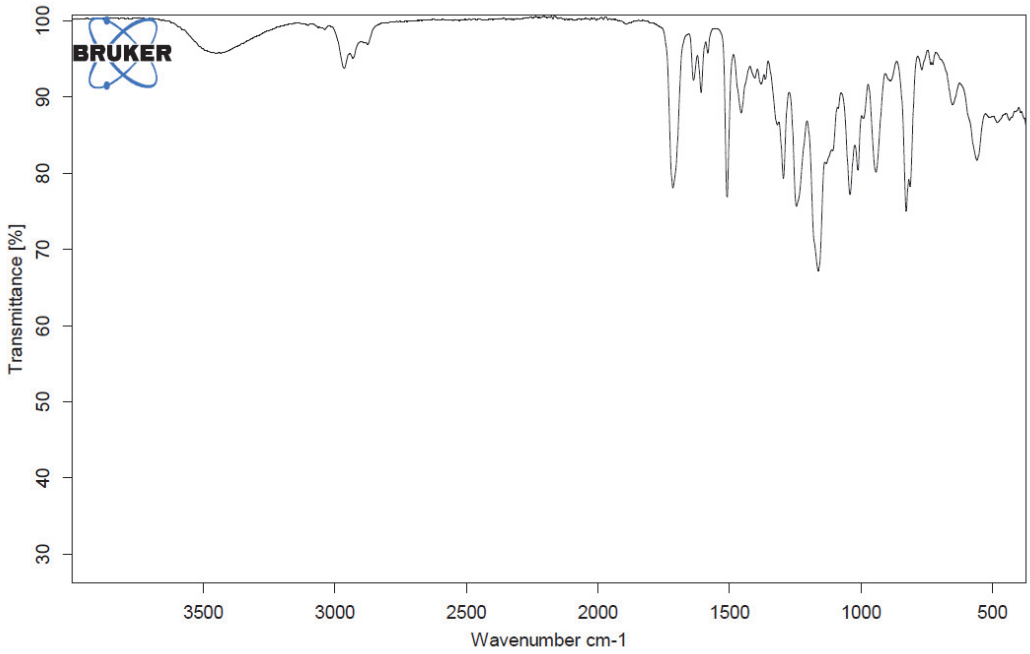
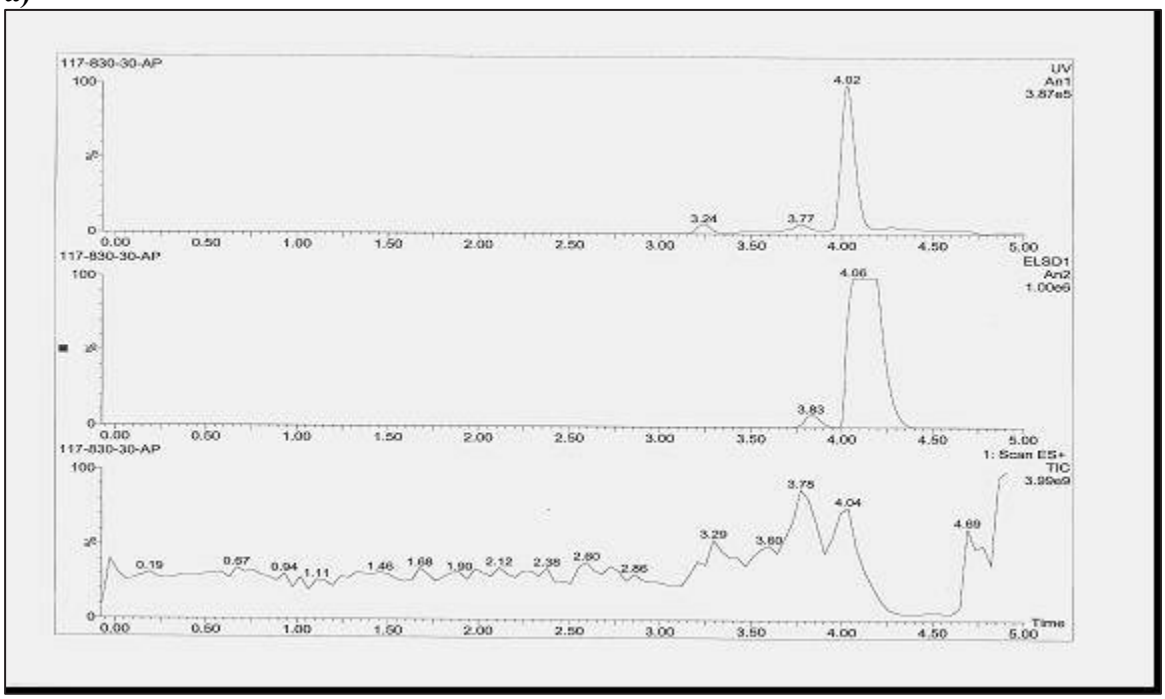


Figure 35 - ATR-FTIR for pure VER monomer

a)



b)

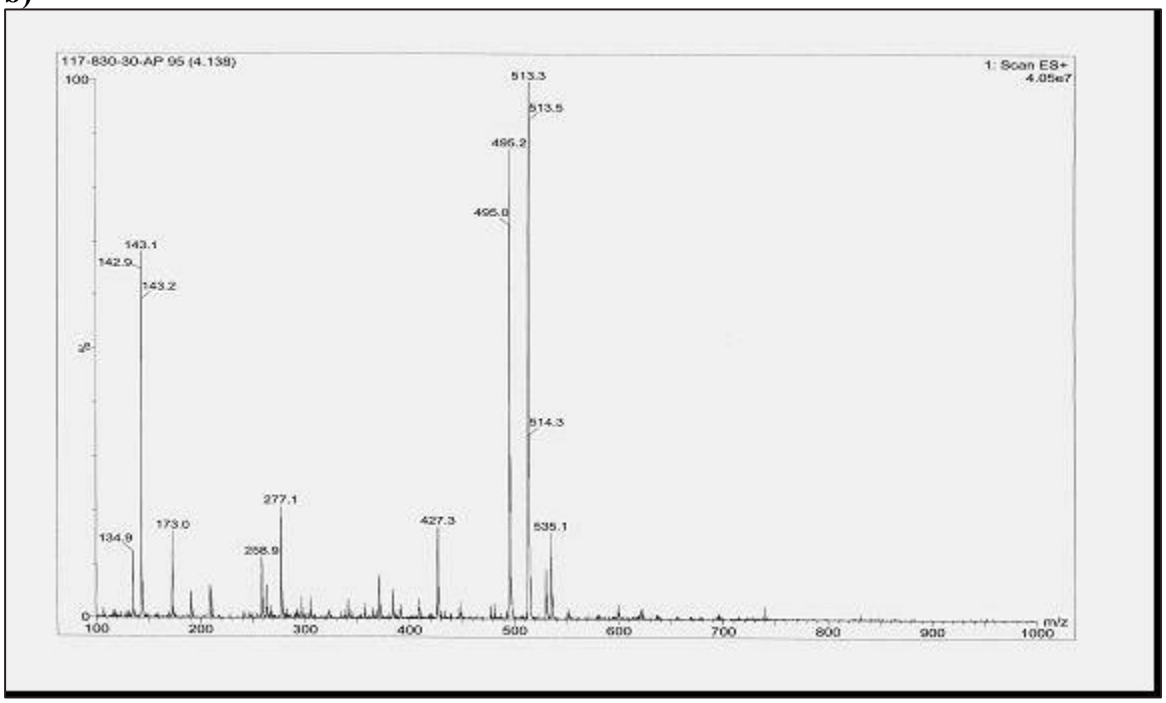
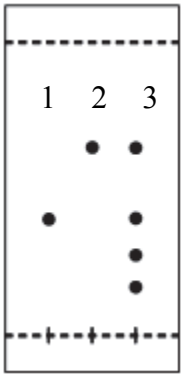


Figure 36 - a) LC and b) MS data acquired for VER monomer

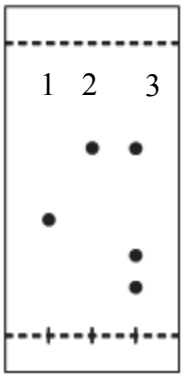
5d.7 Procedure and Results of BPA and GMA, no solvent

BPA (5 g, 0.021 mol) was added to a 250 mL three-neck round-bottom flask and dispersed slowly with GMA (9.4 g, 0.066 mol) in the presence of basic catalyst BDMA (10 µL). The reaction mixture was allowed to stir at 60C overnight. Another round of GMA (9.5 g, 0.067 mol) and BDMA (10 µL) was added at 60C until BPA was completely consumed, which was confirmed by TLC.



1. BPA
2. GMA
3. Product Mixture

Figure 37 - Reproduction of Thin-Layer Chromatogram for VER Synthesis Reaction



1. BPA
2. GMA
3. Product Mixture

Figure 38 - Reproduction of Thin-Layer Chromatogram for Completely Reacted VER Synthesis Reaction

5d.8 VER synthesis reaction scaled up

This scaleup version of the VER synthesis was conducted by adding BPA (20 g, 0.087 mol) to GMA (75 g, 0.5276 mol) in the presence of basic catalyst BDMA in 1L three-neck round-bottom flask equipped with cooling condenser. With a mechanical stirrer the reaction mixture was stirred at 60C with no solvent, until consumption of BPA was confirmed by TLC. The product mixture was then purified by flash chromatography in a gradient ratio using ethyl ether and hexane, conducted by Creagen Bio (Woburn MA).

Milestone: VER Synthesized from BPA and GMA. Initial results from experimental trials indicate that VER monomer was successfully synthesized via reaction of BPA with GMA under basic conditions. Subsequent efforts during the program focused on enhancing the yield of VER monomer by reacting BPA with GMA in the presence of benzyldimethyl amine catalyst and no solvent. This approach was successful in producing VER monomer in high yield and purity. Purified VER monomer was characterized by means of LC-MS, NMR and FT-IR techniques, as illustrated previously.

6. Implications and Relevance of the Results in Addressing Project Objectives

Close examination of the program results and their successful demonstration of feasibility for each individual technical objective reveals that a follow-on program is indeed warranted. The results also showed the need for continued refinement of lignin hydrolysis and pyrolysis reactions in order to increase the yield of purified phenolic products from about 10% to values potentially exceeding 45%. This probability of our meeting the goal is supported by several recent literature references which discussed production of phenolic products from lignin, by means of supercritical water hydrolysis, in overall yields exceeding 50 % [1-19].

7. Conclusions and Implications for Future Research

a. It can be seen that Phase I was a success in determining the feasibility and verifying the methodical ability of synthesizing VER from biowaste materials lignin and glycerin. Success was measured by the completion of the outline objectives 1) isolation of phenol from lignin via hydrolysis of supercritical water, 2) conversion of phenol to bisphenol A, 3) synthesis of glycidyl methacrylate from glycerin via conversion to glycidol and 4) synthesis of vinyl ester resin via reaction of bisphenol A with glycidyl methacrylate, eliminating the use of epichlorohydrin.

b. Objectives for follow-on research.

   The overall objective of the proposed QNA program is to produce vinyl ester resin (VER) from renewable resources, and to produce VER composite-matrix resins, using a low-cost, Vacuum-Assisted, resin Transfer Molded (VARTM) process, for DOD weapon systems that are environmentally compliant during synthesis, processing and application. Controlled microwave irradiation and suitably adjusted pressures will be employed to obtain cleaner products and minimize wastes when nonhomogeneous crude phenolics are used as starting materials and a variety of intermediates are produced in the reaction.

   The resulting sustainable, environmentally safe vinyl ester resin (SESVER) will meet the specifications for VER-based, DoD composite weapons system components that include Naval ship hulls and Army combat vehicles.

   Replacing toxic styrene reactive diluents with less hazardous, nonvolatile methacrylate monomers from biomass in SESVER composite manufacture would provide a significantly safer workplace for manufacturing personnel and cause less harm to our environment.

   Demonstrate that SESVER composite test specimens are comparable in properties and cost to conventional VER/styrene composite test specimens. Substituting biomass starting materials for the manufacture of VER, epoxy and phenolic composite resin matrix would significantly reduce United States dependence on oil.

8. Literature

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