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ABSTRACT

Three general categories of products from the Estonia Kukersite kerogen oil were defined: pure compounds, broad range concentrates, and sweet refinery feedstock. Product development and market research center on these three categories. Further attempts were made to identify and test chemical approaches for producing lower alkyl resorcinols (what the market requires) from higher alkyl resorcinols. The approaches and process conditions tested have not yet produced satisfactory results. Progress was made to interest industry in the phenolic products producible. A sample of oil from the Galoter retort was received from Estonia and characterization of this sample was initiated. The sample was batch extracted and results of yields and selectivity are reported.

Technical Progress Report

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Introduction

To produce samples of marketable quality products, secondary processing of both the extract and raffinate from the extraction step are required. Compositional analysis of the total oil provides a basis upon which to evaluate process steps and to identify promising products. Marketability of the three main product categories will be required to reduce investment risk to acceptable levels. An objective of this phase of the work is to introduce research and product specification results to industry.

Experimental*

GC-MSD Analysis

Conditions and method

GC: HP 5890
Carrier: Helium 0.826 ml/min constant flow
Column: HP-5MS 30m x 0.25mm x 0.25 m
Inlet: 275°C Split mode (50:1), 0.1 μ l neat injection
Oven: 0°C, 5°C/min to 310°C (5 min hold)
Detector: HP 5972A MSD, TIC mode

Procedure

One tenth of a microliter of the kerogen oil, extract, raffinate or other process sample is injected, neat, into a Hewlett Packard model 5890 series II Gas Chromatograph (GC) using a Hewlett Packard model 7673 automatic liquid sampler (ALS). The injection port is pressure programmable and is set for constant flow with an initial pressure of 4 psig and a temperature of 275°C. The injection port is operated in the split mode with the split ratio set at approximately 50:1. This ratio may need to be optimized to give a total ion chromatogram (TIC) with a maximum abundance of 0.5-1.5 million counts. The GC is equipped with an HP-5MS capillary column 30 meters long and 0.25 mm internal diameter. The stationary phase consists of a 5%-Diphenyl-95%-Dimethylpolysiloxane Copolymer with a film thickness of 0.25 micrometer. The Helium carrier gas is flowing at approximately 0.826 ml/min. in constant flow mode. The GC oven temperature is initially set to 0°C and programmed to heat up to 310°C at 5°/min. with a 5 min. final hold. The components are detected with a Hewlett Packard 5972 series mass selective detector (MSD). Extracted Ion Chromatograms (EIC) are generated from the data.ms file as needed for analysis.

Extractions

Liquid-liquid extractions are conducted by one of two methods; batch or semi-continuous. In the batch mode oil and solvent are added in a predetermined ratio (generally about 1:1 by weight) to a separatory funnel, shaken and allowed to equilibrate at a prescribed temperature (generally 50 °C). Once constant temperature is achieved the sample is again shaken and allowed to settle into two phases. The phases are separated by draining the most dense phase (the extract). The

raffinate may be successively extracted with small portions of extraction solvent such that the total amount of solvent used is kept to a ratio of 2:1 or less. The extract portions are combined, solvent is removed by rotary evaporation and the recovered extract is weighed. Solvent is similarly removed from the raffinate and the recovered material is weighed. An overall mass balance for the extraction is calculated. Extracts and raffinates from which solvent has been removed are used directly for analysis and further processing. In the present quarter only batch extractions were conducted.

Aquathermolysis

Aquathermolysis is the thermal cracking of hydrocarbons in the presence of liquid water. Liquid water allows ionic reactions to occur. Feedstock and water are charged batchwise to a high-pressure stainless steel reactor. The pH of the water may be adjusted through the addition of caustic or acid. The system is outfitted with pressure and temperature readouts. An over-pressure automatic release system is also installed. Provisions are made to sample the liquid during reaction through a dip-tube that extends to the bottom of the pressure vessel. A fluidized bed sand bath is preheated to a desired temperature, generally not greater than 350 C. The reactor is immersed in the fluidized bed and the rise in temperature and pressure are monitored. Periodically, a portion (typically 1 to 2 g) of the reactants and products are removed for subsequent analysis by GC-MSD. At the completion of the run a final sample is taken and the reactor is removed from the fluidized bed and allowed to cool.

Elemental Composition

Elemental analysis was obtained through a commercial laboratory that used conventional microanalytical techniques. Oxygen was determined directly and not by difference.

Workup of Raffinate

To specify synthetic crude oil products from Estonia kerogen oil a wet raffinate prepared under task 12(a) was dried. This required fractional distillation in a packed column and stripping of the polar solvent. The dried raffinate will be used as a charge feedstock for catalytic hydroprocessing in a downflow trickle-bed reactor. Process conditions are yet to be determined.

Results and Discussion*

Product Slate

Three classes of products were identified: a) pure compounds, centered around resorcinol and methyl resorcinol, b) broad range (polar) concentrates for use as surfactants, uv absorbers, asphalt additives, etc. and c) sweet refinery feedstock. Production of these types is needed to provide samples for inspection and to assess marketability.

Sweet Refinery Feed

Specification of a sweet refinery feedstock from the Estonian kerogen oil is needed for presentation to regional industries. Specifications will be similar to those for refinery feedstock produced from the USA raffinate. The results of the USA work is shown in Tables 1 and 2, as an illustration of the data needed for the Estonia oil. A crude oil specification sheet is not a complete assay, but gives the audience a sense for the quality in terms of boiling point distribution (crude tower yields) and impurities. In the case of synthetic crude oil from kerogen oil raffinate, the quality will command a premium price because it has already been catalytically hydroprocessed.

Table 1: Boiling-Point Distribution of the KPX Synthetic Refinery Feed
(by simulated distillation)

Fraction	Total, wt.%
Naphtha, <200 C	29.8
Kerosene, 200 - 275 C	16.2
Gas Oil, 275 - 325 C	12.3
Heavy Gas Oil, 325 - 400 C	23.2
Vacuum Gas Oil, 400 -538 C	18.5

Z-BaSICä analysis of Galoter Oil

Approximately 65 kg of Galoter oil was received from the Oil Shale Institute of Tallinn Technical University. The Galoter retorts produce several thousand barrels/day of raw Kukersite kerogen oil and this oil may also be used as feedstock for Value Enhancement Processing, in addition to the Kiviter oil. The Galoter retort operates at a higher severity than the Kiviter retort and for that reason an independent evaluation of this oil must be made.

The Galoter oil was dried by Dean Stark distillation. The oil was found to be surprisingly dry, yielding only 0.4% water. The elemental composition of the raw Galoter oil is given in Table 3.

Table 2: Specification of the KPX Synthetic Refinery Feed

CRUDE PROPERTIES

Gravity, degrees API	36.8
Specific Gravity (60 °F/ 60 °F)	0.841
Total Sulfur, wt. Pct.	0.02
Total Nitrogen, wt. Pct.	0.12
UOP K Factor	12.00
Pour Point, °F	39
Viscosity at 100 °F, cSt	3.3
Vanadium, ppm wt	<1
Nickel, ppm wt	<1
Conradson Carbon, wt. Pct.	nil
Asphaltenes, wt. Pct.	<0.25
Reid Vapor Pressure, psia	n/a
Flash Point, °F	n/a
Hydrogen Sulfide, ppm wt.	nil
Ash Content, wt. Pct.	nil

Table 3 Elemental composition of Galoter oil

Carbon	81.97
Hydrogen	9.68
Nitrogen	0.20
Sulfur	0.74
Oxygen (direct)	7.41
H/C (atomic)	1.41
Density g/cc	0.987

A chromatographic trace of the total oil is shown in Figure-1 and reveals a substantial light end component that is not present in the Kiviter oil (see Figure -2). Analysis of the chromatograms indicates that the Galoter oil contains lower concentrations of resorcinols than the Kiviter oil. However, the elemental composition shows a higher oxygen content for the Galoter oil. Further Z-BaSIC analysis will be required to quantify these differences.

Extraction of Galoter Oil

A sample of total Galoter Oil was extracted by the non-ionic system. The overall mass balance was 22.3% extract and 77.7% raffinate. An elemental analysis of the extract and raffinate were performed. Results (water free) are shown in table 4.

Table 4 Elemental Balance on Galoter oil Extraction

	FEED	CALC. FEED	EXTRACT	RAFFINATE
			Yield Fr. 0.223	Yield Fr. 0.777
C	81.81	81.84	78.79	82.72
H	9.68	9.56	8.63	9.83
N	0.20	0.22	0.42	0.17
S	0.74	0.65	0.77	0.62
O	7.57	7.72	11.40	6.66
H/C	1.41	1.39	1.30	1.42

Results show high enrichment of oxygen in the extract, but less-than-desired recovery. Using a MW of 220 Dalton for the oxygen types and an average of 1.5 oxygen atoms per molecule a coefficient of separation of 0.33 is calculated. These results are similar to those determined for the Kiviter oil (see November, 2000 monthly).

To better understand the cause for lack-of-recovery a chart of partition ratio vs. MW was prepared for the 5-alkyl resorcinols (see figure 3). The partition ratio is the relative concentration of a component in the extract compared to the raffinate. A ratio of 1 indicates there is no preference for the compound between the extract and the raffinate. Results show a strong partition ratio for the lower molecular components, but only about 1.5 for the 5-heptadecyl resorcinol. Given that the yield of extract is only 22.3%, this means that only 34% of the 5-heptadecyl resorcinol is recovered. Clearly, the raffinate maintains strong solvating properties for the oxygen types and work will be needed to find the extraction conditions that inhibit the solubility of the resorcinols in the raffinate.

Further analysis of the separation was conducted on individual species. These results are shown in table -5. The low COS for the higher molecular weight compounds illustrates the nature of the problem. The raffinate is not rejecting enough of the polar compounds, while the extract is solvating too many of the aromatics. This suggests that a target of improving the coefficient-of-separation between the C7 phenols and the methyl phenanthrenes may yield the overall separation desired.

Table-5 Partition Results of Extraction of Galoter Oil

Parameter	single-stage
Process yields (weight percent)	
Extract	22.3
Raffinate	77.7

Partition ratio and recovery results

(Recoveries are shown in parenthesis as weight %)

Light components

C ₁ alkyl naphthalenes	1.01	(22.40)
C ₃ phenols	2.78	(44.38)
Naphthols	3.46	(49.82)
C ₂ resorcinols	21.96	(86.31)

Mid-range components

C ₁ triaromatics	1.06	(23.26)
C ₇ phenols	1.95	(35.93)
Phenanthrenols	2.86	(45.04)
C ₆ resorcinols	5.89	(62.82)

COS results

C ₂ resorcinols - C ₁ alkyl naphthalenes	63.91
Naphthols - C ₁ alkyl naphthalenes	27.42
C ₃ phenols - C ₁ alkyl naphthalenes	21.98
C ₆ resorcinols - C ₁ triaromatics	39.56
Phenanthrenols- C ₁ triaromatics	21.79
C ₇ phenols - C ₁ triaromatics	12.67

Dealkylation

The need for a viable dealkylation step still looms as an important hurdle to cross. Reverse Friedel-Crafts has been proposed as a possible approach. The theoretical basis for this is that in thermodynamically controlled catalytic reactions the reverse reaction should be favored at higher temperatures if the reaction is endothermic and lower temperatures if the reaction is exothermic. The dealkylation reaction is slightly endothermic. However, the dehydroxylation reaction is also slightly endothermic, but less so than the dealkylation reaction. This suggests that higher temperatures will favor dealkylation relative to dehydroxylation, and it may prove that a Friedel-Crafts catalyst would provide a degree of selectivity.

Figure 3 Molecular Weight vs Partition Ratio

Anhydrous AlCl_3 was added at 5.5% weight percent of a total Kiviter extract and gradually heated in a pot still at ambient pressures. Vapor production and overhead liquid production were monitored as a function of temperature. At about 80 °C when the sample softened and the first integral mixing of the AlCl_3 occurred, a strong exothermic reaction was observed, raising the temperature quickly to over 90 °C.

As the temperature was raised periodic liquid samples were taken for GC-MSD analysis. At about 280 °C a small surge of gas production was observed. Above 300 °C reaction water was seen condensing in the condenser. This gave cause to be concerned that dehydroxylation was occurring. The reaction was terminated at 320 °C. Above this termination temperature thermal reactions will occur and would not necessarily be catalytic. In addition to the periodic samples taken, final liquid from the pot was analyzed by GC-MSD. All samples were found to exhibit little change from the starting material.

The interpretation of this experiment is that the catalyst in Friedel-Crafts alkylation does not act as a catalyst for the reverse reaction. This finding is consistent with the mechanism that when alkylating the catalyst first forms carbonium ion from the olefin bond in the alkylating group, and it is this ion that attacks the aromatic ring. The reverse reaction does not occur, apparently because the catalyst is not directly involved with the actual alkylation step.

Literature Search for Dealkylation Reactions

A computer-aided literature search was conducted to identify previously studied reactions for the dealkylation of higher alkyl resorcinols. The literature is remarkably sparse in reactions that pertain to removal of alkyl groups from phenolics. Reverse Friedel-Crafts is mentioned in relationship to alkyl aromatics. A two-step process such as partial oxidation followed by some form of thermolysis is a prospect. Cracking over heterogeneous catalysts was studied for alkylaromatics, but the catalysts were quite exotic. Aquathermolysis showed some interesting results, but the literature on this was 100 to 125 years old, and mass balances were not readily obtained.

The computerized searches looked for reaction by name and empirical formula. References listed in parenthesis are the Beilstein reaction numbers. Examples of other interesting reactions found are: decarboxylation of carboxyl resorcinols in caustic at 250 °C (RX 292067), ring opening of a 4-hydroxy-dihydro-benzofuran to make resorcinol (RX 813691), rearrangement and dealkylation of 5-methyl resorcinol to form mixed phenols (RX 6727329, an 1882 article), cracking of resorcinol oligimer to resorcinol in KOH at 200-230C (RX 7920383), and deacylation of dihydroxy benzaldehyde at 250 °C in H₂O (RX 7920387).

Resorcinol Dealkylation

Many of the aforementioned reactions involved aqueous, caustic systems at temperatures ranging from 100 – 350 C, though none specifically discussed dealkylation of long-chain alkyl groups. It was decided to run some laboratory experiments to see if there was promise in the approach. Because the vapor pressure of 350 C water is 2400 psig, this required careful attention to safety design.

A full-range extract from the Kiviter oil was charged to a high pressure 316 SS batch reactor and the phenols converted to their sodium salts in water. The temperature was quickly raised to 320 °C, which was achieved in 13 minutes and a sample was taken. An intermediate sample was taken when the temperature reached 314 °C (9 minutes into the run).

The samples were acidified, extracted with ethyl acetate and the recovered organics analyzed by GC-MSD. Results are given in Table –6. The data show the change in parent phenol (94), resorcinol (110), what is believed to be mono-substituted phenols (108, carbon numbers 1 to 9) and mono-substituted resorcinols (124, carbon numbers 1 to 12).

Compared to the feedstock material, phenol appears to initially decline, but gains in yield as the reaction progresses. The yield of alkyl phenols also increases with time. Conversely, the higher alkyl resorcinols are cracked in the pyrolysis, but do not result in higher concentrations of parent resorcinol. These results are interpreted as evidence that dehydroxylation of the first hydroxy group on resorcinol is faster than dealkylation. Because the parent molecules (of both phenol and resorcinol) show a greater loss than the higher alkyl homologs at 314 °C of each type, we further conclude that the monohydric hydroxy group is also preferentially lost, compared to the alkyl

groups.

The observation that the parent molecules have a higher yield at the higher temperature than at the lower temperature suggests that the activation energy for the dehydroxylation reaction is lower than that for the dealkylation. Theoretically, this suggests that a flash pyrolysis at higher temperature and shorter residence time would enhance the relative rate of dealkylation compared to dehydroxylation. However, since both are occurring and dehydroxylation is faster at lower temperature, it is unlikely that satisfactory results would be achieved even under flash pyrolysis conditions. For these reasons it was decided to postpone further work using this approach.

Marketing and Industrial Liaison

Efforts are continuing to interest industry in the project and products. Additional meetings have been held with industry with the view of developing a Cooperative Research and Development Agreement (CRADA). It is hoped that a nucleus of industries can be formed as the basis for a consortium of companies with complementary interests. Successful implementation of the Value Enhancement Process approach in Estonia serves as the model for the USA development, and this is a prime objective of the work this year. Prospects identified in recent months are engaged in internal discussions, and there is no additional information to report at this time.

Conclusion*

Higher yields of high value pure compounds are believed necessary for favorable project economics. To obtain these pure compounds from higher alkyl phenols and resorcinols dealkylation is required. Experiments aimed at dealkylation of higher alkyl resorcinols to form resorcinol and methyl resorcinols have, however, produced less than desired results. Private industry interest has been shown in the value-enhancement process approach.

References*

(no references this quarter)

Bibliography

(no bibliography this quarter)

List of Acronyms, Abbreviations and Glossary of Terms

COS – Coefficient of separation. Defined as the mole percent of desired components extracted less the mole percent of non-desired components extracted.

Data.ms file - the computer file generated by the MSD consisting of the ions produced and their intensity (currents) as function of time since injection.

EIC – Extracted ion current, a chromatogram showing the detector response to a particular mass as a function of time since injection, extracted from the data.ms file.

GC – Gas Chromatography, a method for separating volatile components according to their thermodynamically controlled partitioning between a flowing gas phase and a stationary bonded phase.

MSD – Mass Selective Detector, in this case electron impact ionization (70 electron volts) of a quadrupole configuration and having a nominal mass resolution of 1 atomic mass unit.

MW – Molecular weight, expressed in atomic mass units, amu, or Dalton.

TIC – Total ion current, a chromatogram showing the total detector response as a function of time since injection.

Rp – Partition ratio – Defined as the ratio of the concentration of a component in the extract divided by the concentration of that same component in the raffinate. A partition ratio of 1 implies that there is no preference of that component for the raffinate or the extract. In thermodynamic terms, the free energy in both phases is the same.

Aquathermolysis – A term used to describe pyrolysis in the presence of liquid water, as compared with steam pyrolysis, which is a vapor phase reaction.

Carbon number – In this context, the number of carbons found in alkyl groups bonded to a ring system. Thus a C₇ resorcinol would possess seven carbons bonded in various methyl groups or longer alkyl chains to the resorcinol ring.

Galoter – The name given to a type of retort in operation near Narva, Estonia and consisting of a rotary kiln heated by recycled, combusted, spent ore.

Higher alkyl resorcinols – Resorcinols that contain more than 2 alkyl carbons, either as methyl groups or in longer chains. In the case of Estonia kerogen oil the number of total carbons in the highest MW examples is about 16.

Kiviter – The name given to a type of retort in operation near Kohtle Jarve and Kivioli, Estonia and configured as a down-flow vertical chamber heated by cross-flow direct combustion. The Kiviter retort is characterized by a water seal in the bottom zone to cool the produced semicoke

and isolate the retort chamber from the atmosphere.

Lower alkyl resorcinols – Resorcinols that contain 0-2 methyl groups. These types may be separated into pure compounds and markets for these compounds either already exist or can be relatively easily developed.

Value Enhancement Processing – Processing kerogen oil to extract and convert naturally occurring nitrogen and oxygen containing constituents to valuable chemicals. The term ‘enhancement’ pertains to the fact that these same constituents are of very low value as fuel and without the value enhancement processing would result in low production revenues.

Appendices

(none this quarter)

Table 6 Products from Aquathermolysis of Kiviter Extract

FEED				Product #1				Product #3			
				314°C (9 min into run)				320°C (13 min into run)			
Total area	7,159,571,722			Total area	5,382,611,483			Total area	7,609,799,682		
Conc.	19,338	mg/l		Conc.	12,747	mg/l		Conc.	15,299	mg/l	
counts/mg	370,233			counts/mg	422,265			counts/mg	497,405		
				Corr fact	0.876780			Corr fact	0.744330		
ion	No.	Time	Area	Time	Area	Corr area	% of feed	Time	Area	Corr area	% of feed
94	1	10.897	660123	10.937	255585	224091.7	33.95	10.887	1153568	858635	130.1
108	1	14.006	2280610	14.021	657318	576323	25.27	14.029	2910158	2166117	95.0
	2	22.2	1028791	22.229	506499	444088	43.17	22.211	1165758	867708	84.3
	3	24.722	1651580	24.714	1044480	915778.8	55.45	24.72	2345071	1745506	105.7
	4	27.128	1283097	27.112	831270	728840.6	56.80	27.125	1803360	1342294	104.6
	5	29.437	1358216	29.416	1095316	960350.7	70.71	29.436	1846106	1374111	101.2
	6	31.632	1746168	31.613	1611541	1412966	80.92	31.63	2122098	1579540	90.5
	7	33.733	1025031	33.719	767163	672632.9	65.62	33.731	1230096	915597	89.3
	8	35.737	887008	35.722	711080	623460.4	70.29	35.736	996260	741546	83.6
	9	37.671	537977	37.651	545881	478617.3	88.97	37.672	559083	416142	77.4
110	1	20.596	3968098	20.563	2554824	2240018	56.45	20.599	3439106	2559828	64.5
124	1	23.135	61627113	22.983	36426626	31938123	51.82	23.048	11661916	8680310	14.1
	2	27.384	9241689	27.345	6392292	5604631	60.65	27.365	1769377	1317000	14.3
	3	29.631	24164311	29.6	15392878	13496162	55.85	29.62	4009512	2984399	12.4
	4	31.761	45517430	31.72	38813119	34030551	74.76	31.704	8430323	6274939	13.8
	5	33.788	37912365	33.761	35633654	31242861	82.41	33.752	6406700	4768697	12.6
	6	35.783	60736625	35.757	54942885	48172801	79.31	35.736	12685398	9442118	15.5
	7	37.668	59995377	37.643	58090723	50932761	84.89	37.638	12833939	9552681	15.9
	8	39.456	29105480	39.451	25945937	22748868	78.16	39.45	5647723	4203768	14.4
	9	41.196	17032994	41.198	14961337	13117795	77.01	41.204	3212755	2391349	14.0
	10	42.885	11944109	42.89	11648846	10213471	85.51	42.887	2514339	1871497	15.7
	11	44.513	4738652	44.522	5679156	4979368	105.08	44.517	906422	674677	14.2
	12	46.084	2010937	46.096	3033345	2659575	132.26	46.084	736235	548002	27.3

Figure 1 Galoter Oil

Figure 2 Kiviter Oil