

新技術發展報導

A Study of the Origin of Organic Pollutants in Fossil Fuel Production - Part II Interruption and Modification of Pollutant Pathways

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中文摘要：

在論文的第一部份中，有機污染物的生成和根源已以地質化學和石油化學的觀點探討過。在此第二部份中，有關於改良或打消這些有機污染物的方法則被廣泛的討論。這些方法包括制止反應進行、添加物法、前後期處理、和單元操作上的改良。

Abstracts:

In part I of this paper, the genesis and origin of organic pollutants from the geochemical and petrochemical points of view are already discussed. In part II, ways to interrupt or modify pollutant formation during processing by quenching, addition of additives, reaction blocking pretreatment, post-treatment or designed-modification are introduced.

1. Introduction:

In order to be consistent with the definition of pollutants, in the previously discussed Equation 1 through 4, the pollutant species may be expressed by j_i , where $j = 1, 2, 3, 4$. In this manner a copollutant can be 3_i or 4_i . For example, when phenolics react with ammonia, heterocyclic systems containing nitrogen may form. The Bremner-Flaig sequences (1) are illustrated in Table 1. This type of reaction indicates a possible pathway of nitrogenous heterocyclic formation in oil shale production.

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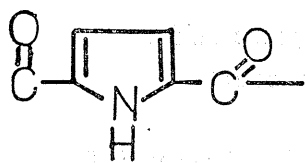
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Coames (2) and Epler et al. (3) showed that for oil shale materials, carcinogenicity decreased with decreasing nitrogen content. Rao et al. (4) showed that for shale oil fractions, the neutral and basic fractions were responsible for the mutagenicity. The basic and neutral fractions of retort water were shown to be refractory toward biodegradation, especially the nitrogenous compounds (5). For this reason, any formation mechanism which led to nitrogen heterocyclics should be blocked as much as possible. One practical approach is to set up an ammonia trap so that the ammoniac reaction cannot proceed. There are many methods to eliminate or reduce ammonia concentration, e.g., stripping, ion exchange, neutralization, and application of vacuum, etc.

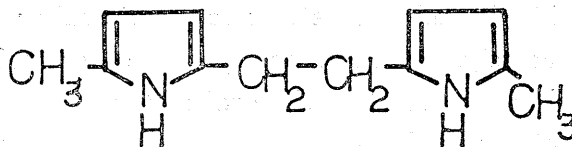
2. Application of Additives:

An important (traditional) additive for shale oil is a pour point depressor that renders it transportable (6). A serious problem with synthetic fuels is the inferiority of the storage stability and the thermal (high temperature) stability. In both cases the oil will deposit enough gum to cause trouble. To meet this need, antioxidants such as phenylene diamine or a hindered phenol (e.g., 2,6-di-*t*-butyl-4-methyl phenol) are added to shale oils and coal liquids (6).

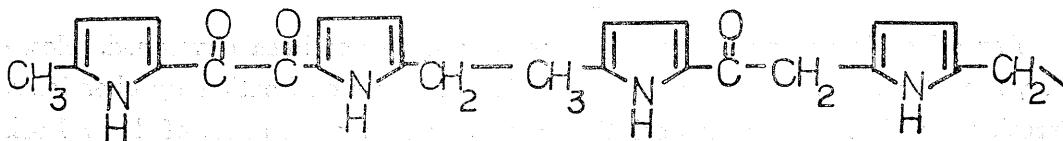
Brinkman et al. (7) stated that the more severe the level of hydrotreating, the more stable the fuel. They found that the polyalkyl pyrroles are strongly deleterious, and the parent heterocyclics are relatively harmless. A plausible mechanism is the polycondensation through the two α -positions, e.g.,



(A)



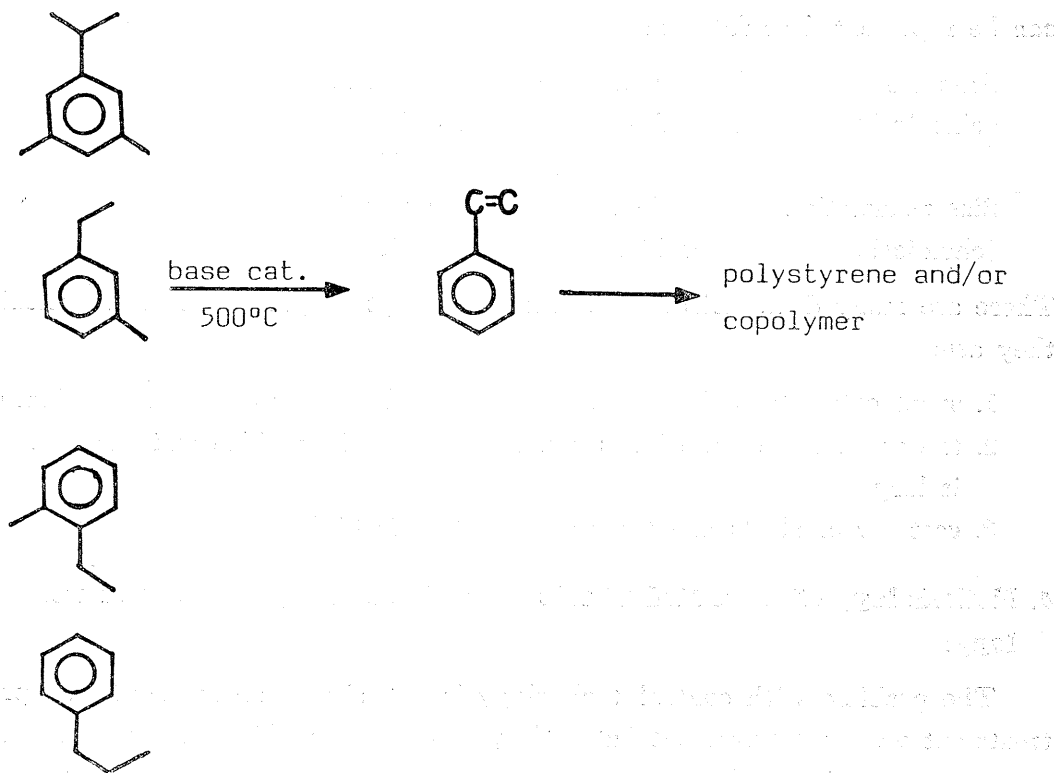
(B)



(C)

(D)

At any rate, the direct scientific input is useful for the process design modification in such a way that will benefit the control strategy. For example, we know that the basic solid surface of CaO and/or CaO/Al₂O₃ or MgO-Fe₃O₃-K₂O system is very efficient for converting a number of alkyl benzenes into styrene and causes extensive polymerization.



The oil shale matrix and spent shale components contain the same basic catalysts. It is possible that extensive catalytic conversion of alkyl benzenes and the copolymerization with the alkenes isolated occur. Experimental observation of a larger oil yield, using the carbonate-free oil shale, and the fact that the delayed coking process yields a large proportion of carbon, tends to support this fact.

Indeed, a fluidized-bed concept for the retorting (23) would solve this problem of excessive carbon formed. In addition the ring cyclization of alkyl pyrrole may be avoidable due to the short contact or residence time. The recent shell pellet heat exchange retorting (SPHER) (24) may have some of these advantages.

5. Conclusion:

In the above analysis, the ways to interrupt or modify pollutant formation

during processing are already pointed out briefly. However, much basic information is needed in order to reassess the design criterion of a new breed of system which combine the engineering process and production and the technology of environmental control. For example, in measuring the thermal (high temperature) stability of synthetic fuels, the method such as the spin concentration (Ng) vs. temperature profile by ESR should be developed (26). Finally, but not the last, I want to thank Dr. Teh-Fu Yen of University of Southern California for his many kindly suggestions on the above work.

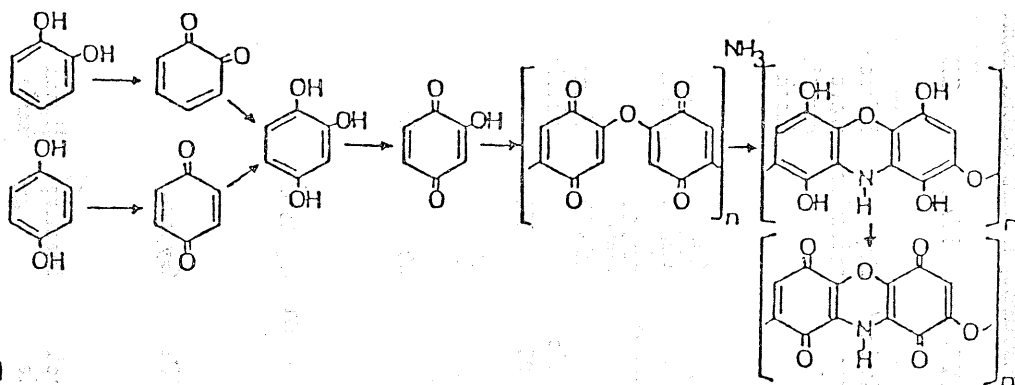
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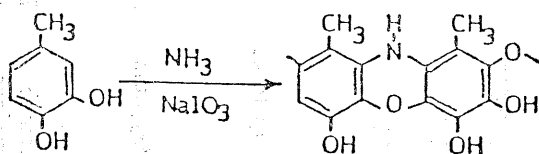
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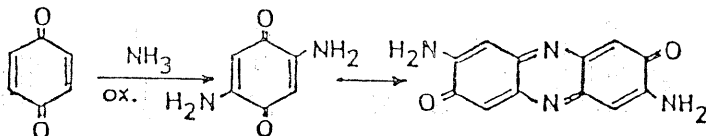
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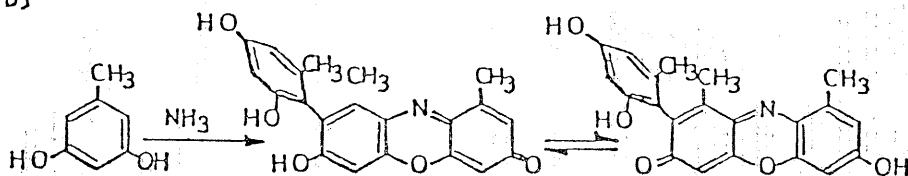
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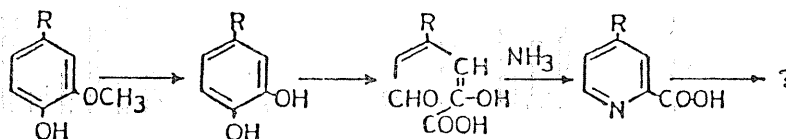


Table 1. Ammonia Reactions with Phenolics (from Yen and Tang, Ref. 25).

TABLE 2. A Summary of the Chemical Desulfurization Processes *Source, Deurbrouck, Ref. 8.

Process	TRW	Magnex	Battelle	Ledgemont	Ames	PERC	JPL	KVB	GE	ARCO
Method	Acid leach	Dry chemi-	Caustic	Oxygen/	Oxygen/	Air water	Chlorine/	Dry	Micro-	Two-
			cal Pre-	ammonia	sodium	leach	water	oxidation	wave	stage
			treatment	leach	carbonate		leach		caustic	cheml-
			plus mag-		leach				leach	oxid-
			netic							ation
			separation							
Reagent(s)	Fe, (SO ₄) ₃ , H ₂ O, O ₂ , acetone	Fe(CO) ₅	NaOH, Ca(OH) ₂ , H ₂ O, CO ₂	O ₂ , H ₂ O, NH ₃ , lime	O ₂ , H ₂ O, Na ₂ CO ₃ , lime	Air, H ₂ O, lime	Cl ₂ , H ₂ O, CH ₃ CO ₃	O ₂ , N ₂ O, H ₂ O, NaOH	H ₂ O, NaOH	
Pressure (psia)	15-80	Atmos- pheric	350-2,500	0-1000	0-1000	500-1500	Atmos- pheric	15-300	Atmos- pheric	
Temperature (°C)	90-135	150-200	220-350	10-230	10-230	150-200	65-05	40-260		
Retention (hr)	1/2-10	1/10-1	1/4-1/2	1/4-24	0-1	0-1	2-4	1		
Pyritic sulfur re- duction (%)	90	90	90	90	90	90	90	90	95	
Organic sulfur re- duction (%)	0	0	Up to 40	Up to 25	Up to 25	Up to 40	Up to 50	Up to 40		40
Sulfur product	Iron sulfates, elemental sulfur	Dry sulfurous mineral matter	H ₂ S, elemental sulfur	Cypsum	Gypsum	Gypsum	H ₂ SO ₄	Gypsum		
Status	Pilot plant, 8 tons/day	Pilot unit, 200 lb/day	Pilot unit, 0.25 ton/year	Inactive	Bench scale	Bench scaled-sign of continuous unit	Bench scale	Inactive	Bench scale	Labora- tory