The separation of hydrocarbon isomers by extractive crystallization with thiourea
by Patrick Joseph Gorton

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in Chemical Engineering
Montana State University

Abstract:
Due to the similarity in their chemical structure, the separation of aromatic hydrocarbons, such as ethylbenzene, and the three isomeric xylenes (para, meta and ortho) was difficult to perform by conventional means. The development of a new technique to effect the separation of these types of compounds was desirable.

Previous research indicated the use of extractive crystallization with thiourea as a possible means of aromatic hydrocarbon separation. This investigation explored this process in further detail, optimizing some of the variables involved.

The extractive crystallization procedure involved contacting a solution of methanol and thiourea with the hydrocarbon feed mixture and with an inductor. The inductor was necessary for the formation of adducts with thiourea and the aromatic system. The resulting mixture was cooled whereupon adducted thiourea crystals were formed. Removal of the crystals by filtration and decomposition by steam stripping yielded an enriched product that was higher in concentration than the feed mixture.

It was determined that methanol was the optimal solvent in terms of separation ability with the aromatic systems. The optimal ratio of solvent to thiourea was found to lie between 2.5 and 5.5 ml/g. Two inductors were studied in depth(1,2,4-trichlorobenzene and 1,1,2-trichlorotrifluoroethane). Equilibrium data was compiled using all possible aromatic combinations with the two inductors. It was shown that the extractive crystallization process compared well against distillation techniques and, in some cases, it far exceeded the ability of conventional distillation. Analyses of the effect of hydrocarbon feed and inductor amounts on separation were also performed.

In summary, it was determined that the process of extractive crystallization in conjunction with the separation of aromatic hydrocarbons was indeed feasible and in some cases, it was much desired over distillation techniques.

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ABSTRACT

Due to the similarity in their chemical structure, the separation of aromatic hydrocarbons, such as ethylbenzene, and the three isomeric xylenes (para, meta and ortho) was difficult to perform by conventional means. The development of a new technique to effect the separation of these types of compounds was desirable.

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INTRODUCTION

The people of the United States have become a society that demands a high standard of living, yet they deplore the current high costs of this standard. Today, as we are becoming more and more energy conscious, industry is faced with the monumental task to provide products at a lower cost to our energy reserve and to still maintain the standards that are set by society.

Within the framework of long-range industrial planning a large area of concern falls within the scope of separation and purification of hydrocarbons. This separation and purification is necessary for the production of synthetics; specifically, those necessary for synthetic rubber, fiber, and chemical plastics. Included in this class of products are the chemical intermediates needed for these materials. This involves the purification or production of isomeric xylenes and ethylbenzene.

Over 90% of the C_8 isomers (1) used in the United States are obtained as a by-product stream from the petroleum reforming operation. A typical analysis of this mixed stream is shown in Table I. The remainder of the isomers produced come from coke-oven byproducts.

TABLE I. AROMATIC C_8 COMPOSITIONS FROM REFORMER(1)

Ethylbenzene	17-20 %
p-Xylene	16-20
m-Xylene	35-40
O-Xylene	19-26

As can be seen in Figure 1, these aromatic isomers find a variety of uses.

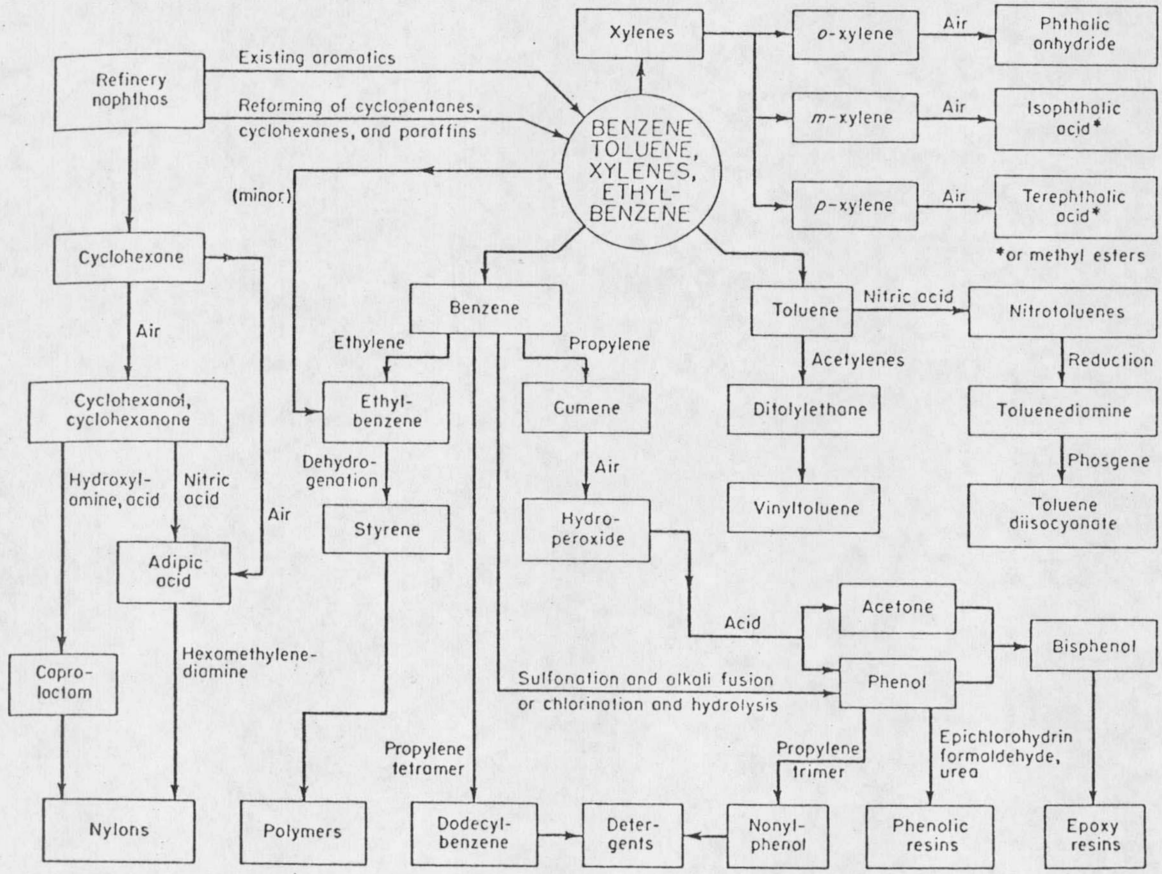

FIGURE 1: PETROCHEMICAL FLOWSHEET(37)

Ethylbenzene, the most widely used of the C_8 isomers, is used almost exclusively in the production of styrene from which polystyrene, polyesters and other plastics are manufactured.

The mixed xylenes are also highly in demand as paint and varnish solvents, as motor fuel octane boosters and as chemical intermediates in the plastics and film industry. The latter industry accounts for a major portion of the total use.

Synthetic fibers have been steadily increasing in world popularity. Recent figures show a yearly growth rate in this industry of over 25% (3). Polyesters, such as Dacron, depend on high purity p-xylene as a chemical intermediate. (99.2% p-xylene is converted to the necessary terephthalic acid used in the polyester fibers and films.)

The most plentiful of the mixed xylenes is used the least. M-xylene finds uses mainly as a gasoline blending agent and as a solvent. The meta-xylene is frequently left in the petroleum stream to be isomerized to other more essential xylenes. A small amount of the isomer is used in the production of isophthalic acid, a chemical intermediate in the manufacture of plasticizers, alkyd resins and other esters.

Essentially, all of the o-xylene isomer is consumed in the production of phthalic anhydride, which is used in dyes, plastics and plasticizers.

Since all of the processes mentioned so far need one specific isomer in relatively high purity, separation of the mixed petroleum stream is necessitated. Several general techniques have been developed for separation of these components; for example, fractional crystallization, extractive distillation and fractional distillation. However, in view of the chemical and physical similarities of the compounds, current research (2) shows that the separation of these isomers is often difficult and costly. In Table II, these similarities can be seen for ethylbenzene and for the three isomeric xylenes (ortho, para and meta).

Current methods of separation of p-xylene include fractional crystallization which removes $\sim$65% of the xylene from the stream. This separation is due to p-xylene's high freezing point relative to the other components. Several other crystallization processes are given in the literature (1),(3). A new and novel approach to this separation, called the Parex process, has been developed by Universal Oil Products. The UOP process is thought to use potassium and barium substituted molecular sieves, which allows selective adsorption of the p-xylene