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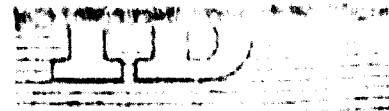
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COMPARISON OF PROCESSES FOR THE PRODUCTION OF AROMATICS^{1/}

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Introduction

The field of industrial chemistry based on aromatic starting materials is a very large one, and to attempt to cover this whole field in general terms would involve a great deal more time than is presently available. This paper is therefore confined to the major starting materials, namely benzene, toluene and xylenes, (BT and X) used in large tonnage petrochemical plants.

The wide variety of processes based on these materials further restricts the scope of this paper to a discussion of the processes available for the separation and purification of the individual pure aromatic compounds, omitting processes such as catalytic reforming and naphtha pyrolysis, in which aromatic hydrocarbons are synthesised from non aromatic hydrocarbons of similar carbon number.

Detailed economic comparisons of the different processes are not provided because of the limited value such comparisons provide. The difference between established processes is often quite small and economic circumstances will vary with location. The intent is to consider the various types of process available and how these can be fitted together in different ways to produce B, T and X.

Some of the most recent processes developed and available commercially are also mentioned.

Sources of Aromatics

The feedstocks generally available for aromatic recovery arise from four main sources, the largest source is from catalytic reforming of suitable naphthas, this operation having mushroomed to keep pace with the demand for high aromatic content motor gasolines. A second source of increasing importance is the by-product "pyrolysis gasolines" originating at the naphtha cracking units for the production of olefins. The traditional coal coking and tar distillation sources are still significant

removed from the solvent by either distillation or re-extraction into some other medium from which they are more easily separated by physical means.

Central to the economy and practicality of a solvent extraction system are, of course, the characteristics of the solvent used.

Important characteristics are:

- (1) The aromatic carrying capacity (i.e. the solubility of the aromatics in the solvent).
- (2) The selectivity of the solvent (i.e. the ability of the solvent to differentiate between aromatic and non-aromatic material).
- (3) The stability of the solvent under the conditions of operation.

In addition the solvent should preferably be cheap, non toxic and non corrosive.

A very large number of solvents have been proposed and most represent a compromise between aromatic carrying capacity and selectivity. Solvents with a high carrying capacity usually have a lower selectivity, and many proven systems use the addition of a third component, e.g. water in glycol or sulfolane, to increase the selectivity at some loss in carrying capacity.

Generally viable solvent extraction processes have used as solvents ethylene glycol, sulfolane, N-methyl pyrrolidone (NMP), dimethyl sulphoxide (DMSO) and formyl morpholine. Propylene carbonate and dimethyl fumarate have also been proposed.

The best known of the solvents is probably ethylene glycol which has been widely used in the Udex process, however, glycol has been largely

superheated by sulfolane and a large number of 20x units have been modified to operate with sulfolane as solvent. The sulfolane process has been used as an example to display the principal aspects of a solvent extraction unit and the following process description should be read in connection with the simplified flow diagram shown in Figure 1.

The feed is a reformate containing about 50% by volume of aromatics, the aromatic stream being fed to the base of the extraction column together with 'lean wash' or 'reflux' solvent. Solvent from the base of the extraction column is heat exchanged with the 'lean' solvent and then to other heated extract to provide a level of saturation which runs before the rich solvent to strip it to recover the sample component. Water also runs counter-current to the aromatic stream to separate it by displacement and to wash the raffinate from the extraction column to recover sulfolane solvent reducing the loss of solvent from the system.

The sulfolane unit as shown would be expected to recover over 99% of the toluene, 98% of the toluene and 96% of the xylenes present in the feed.

The process scheme for sulfolane can of course be used with other solvents but temperature, pressure, etc. of the system will change as will the total sizing and number of equipment items.

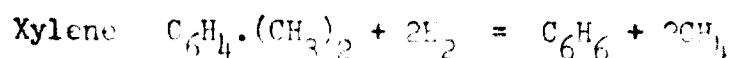
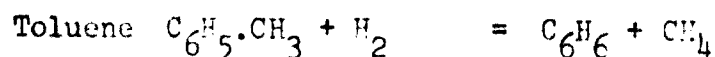
Processes using re-extraction of the aromatic extract into a secondary solvent prior to distillation, such as the EIP process using Dimethyl sulfoxide as primary solvent, also the Permex process, do so primarily to avoid solvent degradation under the high temperatures necessary to strip the extract from the solvent. The flow diagram for this type of process is attached in Figure 2.

Hydrotreating Processes

Feedstocks with high aromatic content arising from pyrolysis processes contain a high percentage of the non aromatic hydrocarbons as olefinic and diolefinic material. Before these feedstocks can be handled to recover the aromatic fraction in the type of process under review, it is necessary in many cases for the feedstock to be pretreated to remove all unsaturated material. This is generally effected by a two stage catalytic hydrogenation, the first stage generally being in the liquid phase to selectively hydrogenate the diolefins, the second stage the vapour phase hydrogenation of the olefins to the corresponding saturated hydrocarbon. Sulphur compounds present in the feedstock may also be converted to hydrogen sulphide during the second stage of hydrogenation.

Hydrodealkylation

These processes were developed initially to convert unwanted toluene into the more saleable benzene by removal of the methyl group from the aromatic ring. This principle applies to other poly substituted aromatics, the alkyl groups being removed to produce benzene and the corresponding paraffin, e.g.



Dealkylation of xylenes is not generally an economic proposition due to the initially high intrinsic value of the xylenes and the low yield of benzene with the correspondingly higher consumption of hydrogen.

However, other side reactions occurring sometimes can be used to justify dealkylation of the higher poly substituted benzenes by virtue of the simplicity of the process unit. The main side reaction occurring in the operating region of dealkylation is the hydrogenation of non aromatic hydrocarbons to low boiling paraffin gases, generally methane and

ethane, with the same rate of alkylation is observed as in the presence of a catalyst, and C_{10} hydrocarbons are produced in appreciable yield with consequent reduction in hydrogen consumption, etc.



Concentration of Lewis acids such as $AlCl_3$ or $SnCl_4$ or aromatic such as nitrobenzene, toluene, diphenyl ether, etc., but these are generally inhibited by alkylation to minimize the yield to achieve the equilibrium composition of the products.

There are a large number of sensitive hydroalkylation processes available, but basically involve heating the feedstock admixed with hydrogen to temperatures in the range of 1000 - 2000° F at pressures of 100 - 1000 psi. The reaction products are cooled and separated into several various fractions. The unreacted hydrogen, unused hydrocarbon, and unreacted hydrogen are recycled. The liquid fraction is fractionated to yield high purity benzene, the remaining unreacted aromatics being recycled to alkylation.

Hydroalkylation processes fall into two categories, namely catalytic and thermal. Catalytic, Lit. 1, Pyral, Hydral and text 1 processes such as, UOP, Shell, and thermal processes such as HDA from Atlantic Refining and HPI, the IBC process of Mitsubishi Chemical and the UOP process developed by the Shell Development and Refining Co.

There is a growing tendency to produce aromatic rich materials with a reasonably high aromatic content, particularly pyrolytic gasolines. The alkylation of the aromatic fraction is highly exothermic and the alkylation processes are now better suited to handling the inherent high temperature rise than the catalytic processes.

The back mixed thermal reactors developed by Mitsubishi and the Gas Council have a major advantage over the plug flow type of reactor for

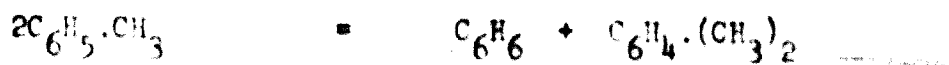
certain feedstocks of high non aromatic content, the isothermal characteristic simplifying control of the reaction temperature rise by using the feedstock preheat as quench for the reaction. The DRU reactor developed by the Gas Council has been used commercially in about fifty applications hydrocrackinging naphtha to petrol, the simplicity of control of the reaction being demonstrated by the thermal stability of these reactors in operation.

The processes of catalytic reforming and thermal dealkylation can be integrated to produce benzene and fuel gas, the hydrogen requirement is, however high, and the aromatic fraction only economic where a cheap hydrogen source is available, or fuel gas can be sold at a substantial credit. Integration of dealkylation unit with naphtha cracking units can benefit the overall economics of the cracker by increasing the ethylene output, (by recycle of the paraffinic fraction of the pyrolysis gasolene as either or propane/butane) and the aromatics are produced as either benzene or a range of BT and X.

Disproportionation and Transalkylation

These are relatively new processes which deserve more attention than they have so far received

Disproportionation is the reaction of two molecules of the same hydrocarbon to yield one molecule each of the next higher and lower homologues. As applied to toluene the reaction results in the formation of benzene and mixed xylenes.



Processes of this type have been developed by Sinclair Research Incorporated and Toyo Rayon. In the Sinclair process the yield of benzene and xylene is about 97% of theoretical. A typical material balance for a 1500 barrel a day plant is shown in Table 1.

Transalkylation involves the transfer of an alkyl group from a poly-alkylated aromatic ring to a less substituted aromatic ring. An

example would be the transfer of one methyl group from trimethyl benzene to toluene to produce mixed xylenes.



In the production of paraxylene by isomerisation some C₉ and higher aromatics are produced and their alkylation is of a very economic nature. Separation of the heavy material to valuable mixed xylene feedstocks is a typical by-product of the isomerisation process in which 10-15% benzene and 2% toluene is transferred with different quantities of C₉ and C₁₀ aromatics.

Table 1

Estimated Toluene Displacement Yields

	<u>Feed</u>	<u>Product</u>
	<u>MPCD</u>	<u>MPCD</u>
Benzene	-	615
Toluene	1500	-
Xylenes	-	840
Gas	-	23*
Coke	-	22*
	<u>1500</u>	<u>1500</u>

*Toluene equivalent.

Table 2

Sinclair Transalkylation Process

Estimated Yields

Feed, B/SD	I	II	III
Toluene	1500	1500	1500
C ₉ + Aromatics	0	1000	1500
Products, B/SD			
Benzene	615	550	290
Xylenes	840	1860	2605
Gas*	23	45	53
Coke*	22	45	52

*B/SD Feed Equivalent

Gas Fuel Value approx. 23,000 BTU/LB

Coke Burn Heat Recovered for Net Steam Make

Both transalkylation and disproportionation can be employed over a wide range of feedstock compositions. They are most economical when integrated with other aromatic producing processes.

One of the most spectacular growth products of the 1950's and 60's has been polyester fibre. It is almost universally made from terephthalic acid or dimethyl terephthalate, which are in turn derived from paraxylene. The growth of paraxylene itself has therefore been equally dramatic, as table 3 shows

Table 3 Paraxylene Production

Capacity - U.S.A.

<u>Year</u>	<u>Plant Capacity</u> <u>million lb/year</u>
1960	1
1952	8
1955	70
1960	140
1967	900
1970	2000

This growth would not have been possible without the development of economic processes based on petroleum raw materials.

Feed Preparation

Paraxylene occurs along with ortho- and meta-xylene and ethyl benzene in a variety of aromatic hydrocarbon mixtures, but it is mainly recovered from catalytic reformate. Along with benzene and toluene, the xylenes are separated from paraffins by solvent extraction. Benzene and toluene are then separated by distillation, leaving an aromatic C_8 mixture. An alternative method which may become economic where only xylenes are required (and is in fact used in a recent Power-Gas plant) is to prepare a closely fractionated C_8 mixture from reformate and then separate the aromatics from it by extractive distillation.

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Isomerisation

The noble metal catalysts (e.g. platinum) are best at isomerising ethyl benzene, and are also capable of long periods on line without regeneration. On the debit side, they are expensive to install. Also since carbon laydown on the catalyst is prevented by using a high partial pressure of hydrogen in the reactor, a hydrogen supply is required. Noble metal isomerisation processes are licensed by Engelhard Atlantic Octafining and HOP.

A quite different type of isomerisation process is based on silica-alumina type cracking catalysts. These are cheap, but need frequent regeneration and therefore twin reactors. Such processes have been developed by ICI in the UK and Aruzan in Japan. Silica-alumina catalysts do not isomerise ethyl benzene to any appreciable extent and any ethyl benzene present in the feed must therefore be removed by distillation either before or after isomerisation. This is in fact not a serious problem, because isomerisation processes tend to produce some light and heavy ends, which have to be distilled out anyway. The same distillation columns can be used to prevent ethyl benzene from building up in the system.

Recently, a new family of isomerisation processes have emerged, typified by Esso Isofining. Like Octafining, the Esso process uses hydrogen to give long catalyst life between regenerations, but the catalyst is much cheaper to install. The Esso process is also claimed to give higher aromatic yields. It cannot, however, isomerise ethyl benzene.

Crystallisation

Most crystallisation processes use centrifuges to separate paraxylene crystals from mother liquor, but a number of variations have been tried.

Some processes use a continuous vacuum filter in the first stage. One or two additional crystallisation stages are needed to purify the paraxylene, the purity of which has increased in recent years from 95% to 99% and even more. Sometimes a light hydrocarbon, such as pentane, is used to wash mother liquor off the paraxylene crystals in the centrifuge, and is then subsequently removed by distillation.

A novel approach to paraxylene purification has been developed by Phillips, with the 'pulse column'. This is an ingenious countercurrent device in which a moving bed of impure paraxylene crystals is continuously purified and washed in a reflux of pure paraxylene. The crystal bed is kept moving by a pulse pump which shakes the bed very rapidly or twice to stop it freezing solid. A recent ICI plant uses this process on quite a large scale. Other crystallisation processes are owned by Amoco, Maruzen, Antar, Chevron and Sinclair.

New Processes

Quite recently two processes have been announced which separate xylenes in a quite different way.

The first of these is Japan Gas Chemicals' metaxylene extraction process. A mixture of HF and BF_3 forms a complex with m-xylene and completely removes it from the C_8 mixture. The remaining ethyl benzene, ortho- and paraxylene can then be separated by distillation. m-Xylene can be recovered from the BF_3 complex in 99% purity. This process is perhaps most applicable where metaxylene is required as a pure product, but all or part of the metaxylene can be isomerised to ortho- and paraxylene. It is unfortunate that the market for m-xylene is much more limited than for the other C_8 's, so that isomerisation is usually necessary. The new process has been commercialised on a fairly large scale in Japan.

The other new process is UOP's 'Parex' process. This uses a solid adsorbent to extract paraxylene instead of crystallisation. It can be used with any isomerisation process and has two great advantages over crystallisation. First, it recovers almost all the paraxylene in the feed, instead of only half, so that the recycle to isomerisation is much reduced. Secondly, it avoids the low temperatures (down to -90°C) and solids handling problems of crystallisation processes.

Since Parex separates essentially all the paraxylene, m-xylene can be recovered by distillation from the material recycled to isomerisation. Studies by the authors indicate that the Parex process is likely to be somewhat cheaper than crystallisation provided full advantage can be taken of the reduced recycle to isomerisation.

Conclusion

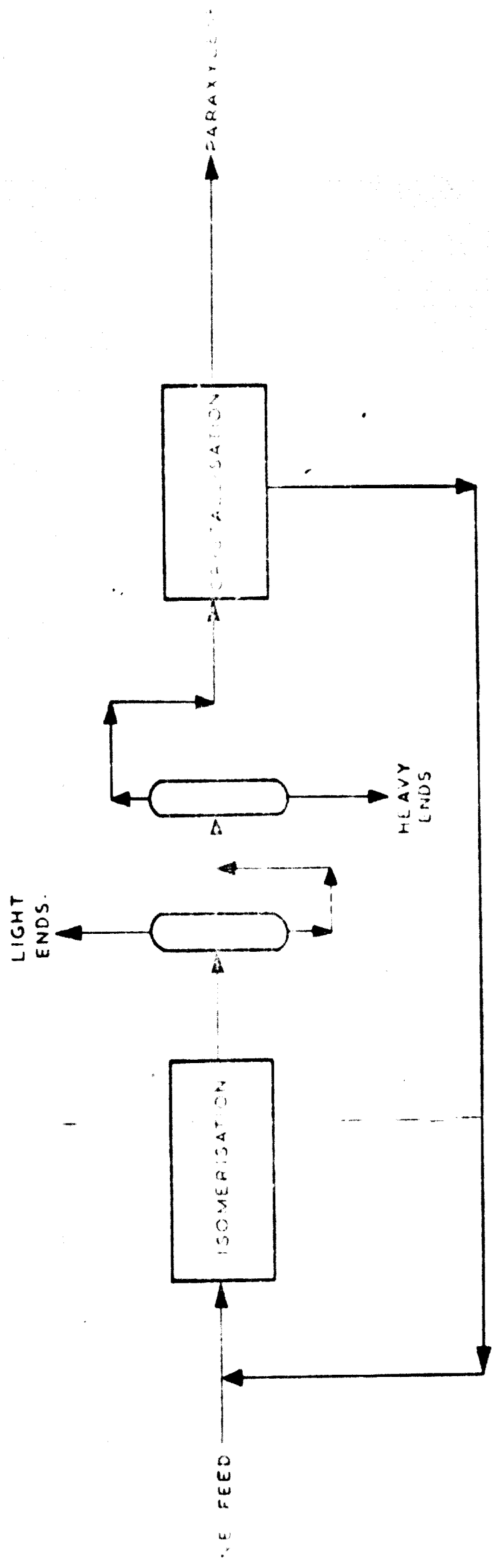
The production of primary aromatic compounds from petroleum based feedstocks is of major and growing importance.

Technology in this field is still developing and a number of interesting new processes are becoming available, that will provide flexibility in product quantities with ensuing lower production costs.

Examples of these are :

- (a) The use of pyrolysis gasolene as a feedstock for BT and X recovery by hydrogenation.
- (b) Transalkylation and disproportionation techniques to produce aromatics, particularly xylenes.
- (c) New paraxylene processes based upon solvent extraction and adsorption.

Finally it is clear that there is no single process which is most appropriate to all cases. An intending new producer must choose carefully from a wide range of process to be the most appropriate technology for use in local circumstances.



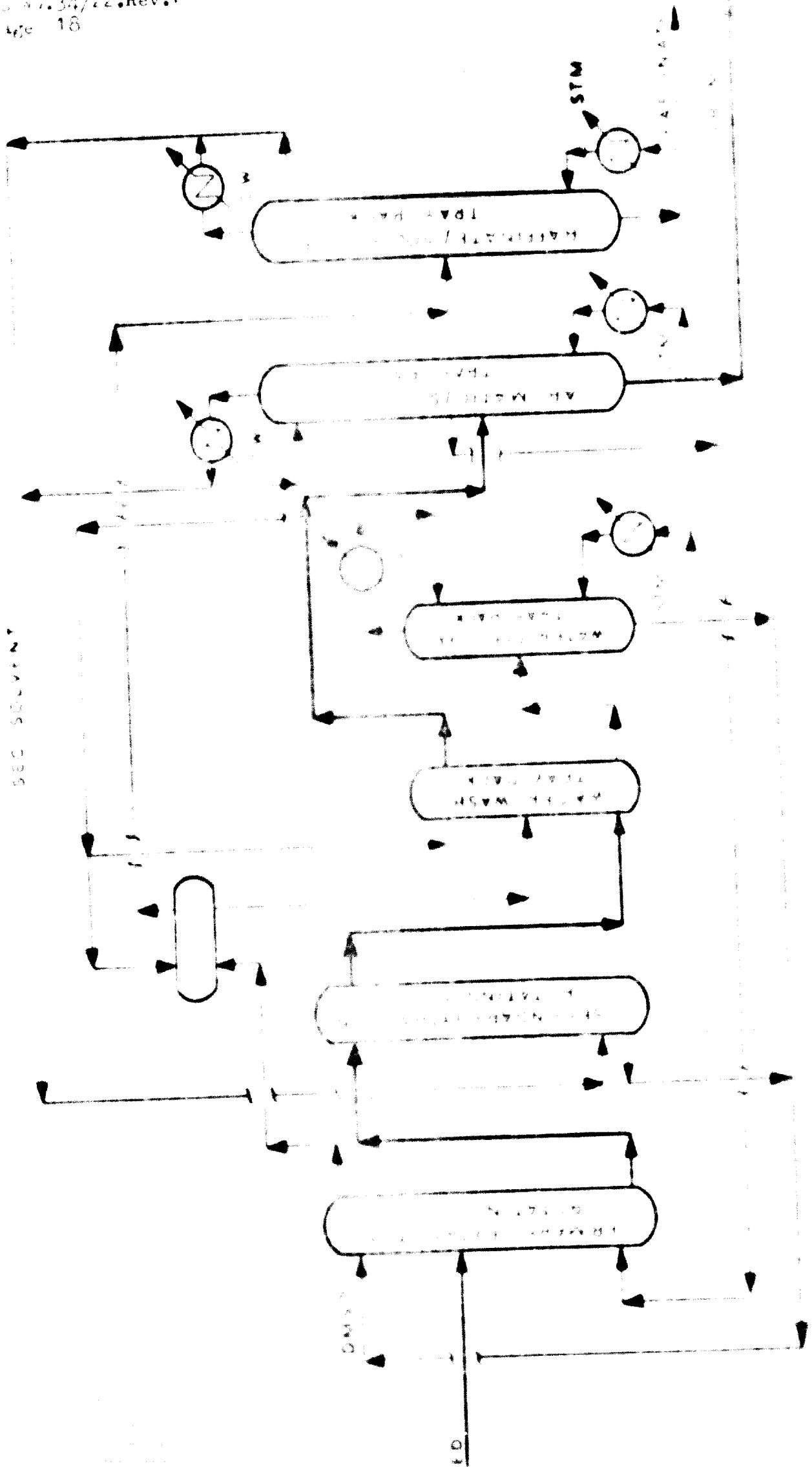


FIG. 10

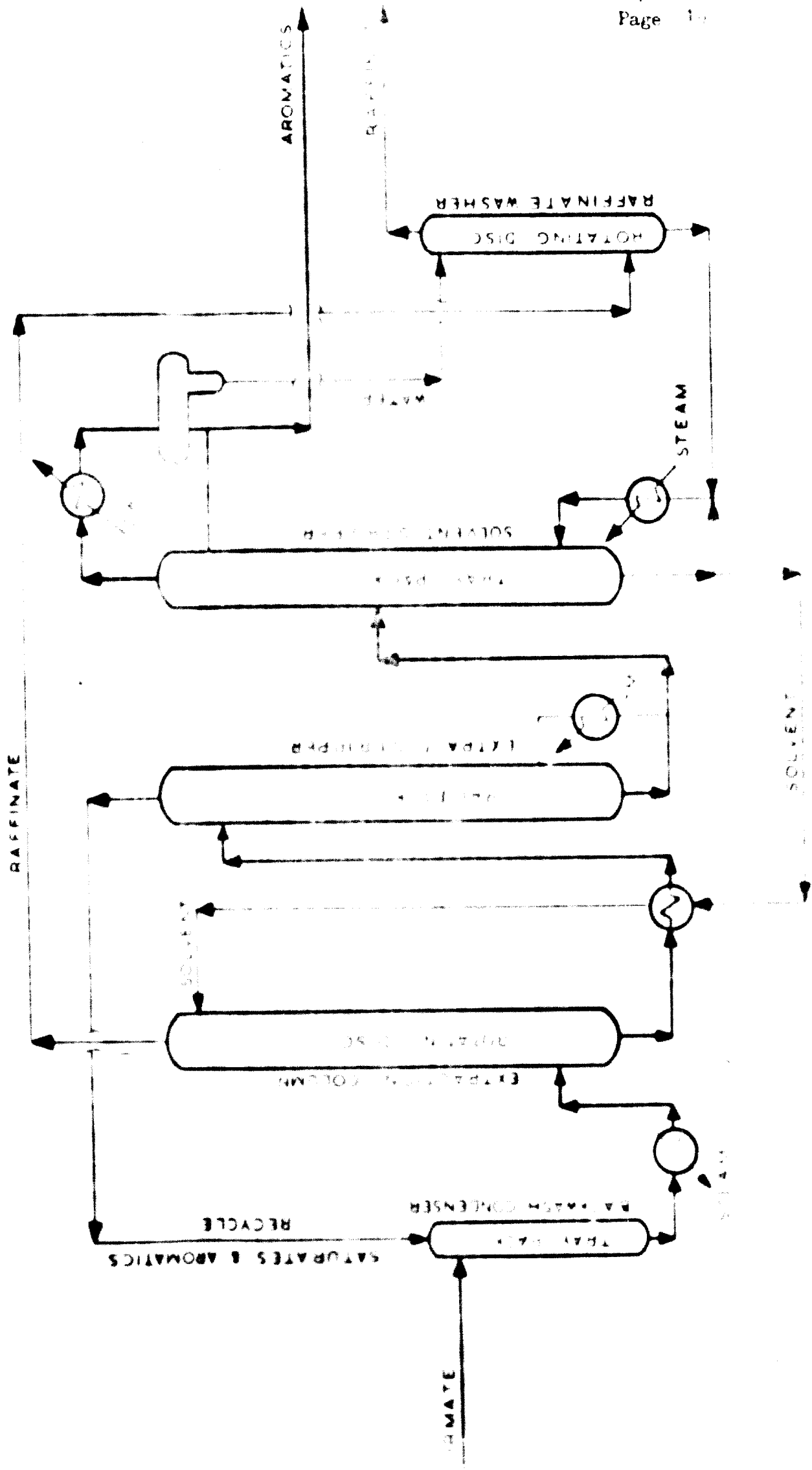
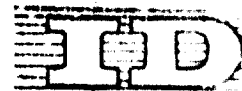


FIG. 1. SOLVENT STRIPPER WITH SIMPLE FLOW DIAGRAM



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SUMMARY

COMPARISON OF PROCESSES FOR THE PRODUCTION OF AROMATICS ^{1/}

by

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The paper deals only with the primary alkyl aromatics namely benzene, toluene, xylene and ethylbenzene. No discussion is conducted on the production of other aromatic compounds such as phthalic anhydride, terephthalic acid etc.

Emphasis is placed upon processes for the separation of aromatic hydrocarbons from non-aromatic material and in the conversion of one type of aromatic compound into another. The production of aromatic compounds from other non-aromatic material is either reforming or pyrolytic cracking type of reactions is not considered in detail.

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The various sources of aromatic hydrocarbons are surveyed and reference made to the changing trends in separating aromatic compounds from complex mixtures.

Solvent extraction processes are described generally and some qualitative remarks made about the suitability of processes and their solvents.

Alkylation processes are beginning to find wider application in the production of aromatic material and ways in which this technique is being applied to other feedstocks are described.

Some of the newer processes in the aromatic production field are described and compared with their more conventional counterparts. In particular, the techniques of transalkylation/disproportionation and two new paraxylene processes are described.

It is concluded that there is no single process which is in all circumstances the most appropriate process i.e. each circumstance must be examined on its own merits for the most suitable application of an increasingly large range of process technology.





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