

Report Abstract

Linear Alkylbenzene (LAB)

Production Costs & Technology for UOP DETAL and HF (Pacol, Define, PEP, Alkylation), EniChem/SASOL Monochloroparaffins LAB processes; and UOP (Molex) & ExxonMobil Chemical recovery) n-paraffins routes. Environmental/Health Risk Assessment & Regional Supply/Demand Forecasts.

PERP07/08S7

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CHEMSYSTEMS PERP PROGRAM

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For further information about these reports contact Dr. Jeffrey S. Plotkin, Vice President and Global Director, PERP Program, phone: 1-914-609-0315; fax: 1-914-609-0399; e-mail: jplotkin@nexant.com; or Heidi Junker Coleman, phone: 1-914-609-0381, e-mail address: hcoleman@nexant.com, Website: <http://www.chemsystems.com>.

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INTRODUCTION

The new edition of the Linear Alkylbenzene (LAB) PERP provides the reader with a complete overview and analysis of technologies, economics and commercial/market perspective.

The commercial development of LAB focused on the extraction of high purity linear paraffins derived from hydrotreated kerosene feedstock. These linear paraffins were dehydrogenated to linear internal mono-olefins. Using a catalyst, the dehydrogenation effluent was used to alkylate benzene to produce LAB. The resulting LAB product became the synthetic detergent intermediate for the production of linear alkylbenzene sulfonate (LAS), a major biodegradable synthetic surfactant which replaced dodecylbenzenes having slow rates of biodegradation in the 1960s. LAS remains the dominant workhorse surfactant but its position in North America and Western Europe is constantly challenged by detergent alcohol derivatives, as described in the commercial section.

In the technology section, commercially practiced processes for the production of LAB and *n*-paraffin is described and detailed. In the LAB arena, several LAB production processes are reviewed. The emphasis is on the DETAL and UOP HF processes as these are the dominant technologies in the LAB industry today. Some new developments in improved catalyst performance for DETAL are also reviewed for comparison against traditional routes. An update on current LAB and LAS environmental/health risk assessments is given.

In the process economics section, there are two distinct economic analysis offered. One analysis focuses on the *n*-paraffin production from kerosene comparing the UOP with the ExxonMobil route. The second analysis evaluates LAB production from three routes: UOP DETAL, UOP HF/*n*-paraffin, and HF/olefins. Manufacturing economics for the route employing aluminum chloride is described in the previous LAB PERP report, 01/02S8, since this process is being phased out.

TECHNOLOGY

LAB has emerged as the dominant detergent intermediate since the early 1960s driven by the environmental need to produce biodegradable detergents.

Commercially, in the past, there were two major catalysts for the alkylation of benzene with higher alpha or internal mono-olefins (C₁₀-C₁₆ detergent range olefins), hydrogen fluoride HF and AlCl₃. The HF-based process became more prevalent than ones based on aluminum chloride. The potential for accidental release of hydrofluoric acid raised environmental concerns (Clear Air Act Amendment) and, with the introduction of a solid catalyst system in 1995, commercially known as the DETAL process, which eliminates the problem of catalyst neutralization and disposal of HF, the LAB industry has adopted the solid catalyst-based process as the “preferred process”. Since 1995, most of the new LAB plants that have come on stream have employed the DETAL process.

The five routes used to produce LAB commercially are detailed in the report:

- Dehydrogenation of *n*-paraffins to internal olefins followed by benzene alkylation using HF catalyst (UOP/HF *n*-Paraffin Process).
- Dehydrogenation of *n*-paraffins to internal olefins followed by benzene alkylation using a fixed-bed catalyst (DETAL).
- Chlorination of *n*-paraffins to monochloroparaffins followed by benzene alkylation with aluminum chloride (AlCl₃) catalyst (Friedel-Craft Alkylation).
- Chlorination of *n*-paraffins to monochlorinated paraffins followed by dechlorination to produce olefins and subsequent benzene alkylation (process is however no longer commercially employed).
- Purchased olefins reacted with benzene in the presence of HF or AlCl₃ catalyst.

A discussion on advancements in LAB alkylation catalysts, including for example UOP layered catalysts, ionic liquids, supported AlCl₃ catalysts, zeolite catalysts and next generation Detal alkylation catalyst.

A complete analysis of LAB commercial routes must include a discussion on the *n*-paraffins commercial routes since there are some integrated LAB producers who start from kerosene as raw material but there are other LAB producers who purchase *n*-paraffins. Thus detailed process descriptions of the UOP and ExxonMobil commercial processes available for *n*-paraffins production are given and compared:

- The UOP process for producing normal paraffin is made up of three units: a kerosene prefractionation unit, a hydrotreating unit and a MolexTM unit.
- ExxonMobil Chemical technology includes a Recovery process and can produce LAB grade *n*-paraffins from most medium to low sulfur kerosene without the use of a hydrotreater stage upstream. At high sulfur levels a Purification process is added to produce a high quality *n*-paraffin product.

The more pertinent LAB Production Technologies discussed and evaluated in the report include:

- The UOP HF/*n*-Paraffin process comprises several units/stages:
 - PACOL Stage: where *n*-paraffins are converted to mono-olefins (typically internal mono-olefins)
 - A DEFINE Unit: whose primary function is to convert residual diolefins to mono-olefins
 - A PEP Unit: essentially an aromatic removal unit is introduced before the alkylation step to improve LAB yield and quality
 - An Alkylation Step: where mono-olefins, both internal and alpha olefins, are reacted with benzene to produce LAB in the presence of HF catalyst.

- The UOP DetalTM/*n*-Paraffin Process has several of the stages depicted in the UOP HF process, but it is principally different in the benzene alkylation step, during which a solid-state catalyst is employed. Also discussed is the UOP and Cepsa developing transalkylation (TA) stage to the Detal process wherein any higher alkylated benzenes (HAB) are contacted with additional benzene over a transalkylation catalyst.
- The chlorination of *n*-paraffins to form monochloroparaffins followed by alkylation with benzene which is one of the oldest commercial routes for the production of LAB. EniChem Augusta SpA, now Sasol, has developed a route which involves the alkylation of mono-olefins with benzene in the presence of aluminum chloride catalyst.

Each of the LAB processes creates LAB products with different product and application features. Important product characteristics include the bromine index, sulfonatability, amount of 2-phenyl isomers (2-phenylalkane), amount of tetralin content, amount of non-alkylbenzene components, and the linearity of the product. A comparison of product characteristics from the four process routes still in commercial operation is given.

PROCESS ECONOMICS

The following **Normal Paraffins** Production process economics have been evaluated:

- UOP Hydrotreater/Molex Complex Cost of Production Estimate for: Normal Paraffins Process
- ExxonMobil Chemical Recovery and Purification Cost of Production Estimate for Normal Paraffins Process

The following **LAB Production** process economics have been evaluated:

- **UOP PACOL/DEFINE/PEP/HF** Alkylation Cost of Production Estimate for Linear Alkylbenzene Process
- **UOP PACOL/DEFINE/PEP/DETAL** Alkylation (**UOP New Development**) Cost of Production Estimate for Linear Alkylbenzene Process
- Alpha & Internal Normal Olefins/HF Alkylation Cost of Production Estimate for Linear Alkylbenzene Process.

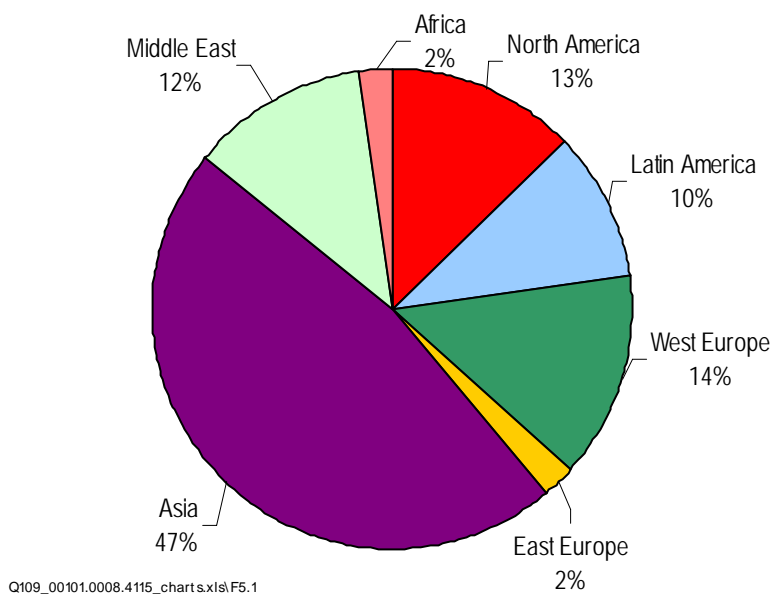
The sensitivity of the *n*-paraffins and LAB economics has been examined for variations in capital investment, variation in capacity (e.g., economy of scale) and variations in feedstock (kerosene, benzene) price. Also, the cost of LAB is examined for its sensitivity to the *n*-paraffin transfer price for the Detal and HF processes.

COMMERCIAL ANALYSIS

The commercial section provides a detailed understanding of the regional and global market dynamics for this key detergent intermediate. In addition to capacity and demand, supply/demand balances have been developed for all the major regions. For North America, Western Europe, and Asia Pacific details of LAB capacity by Producer and Process for the years 2005-2007 are given.

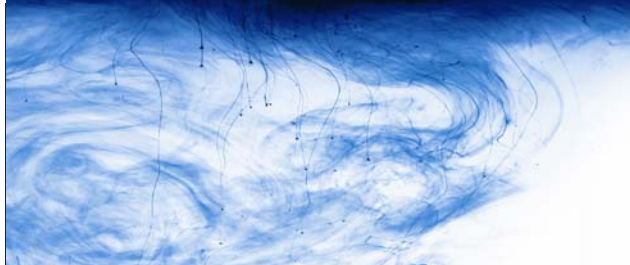
The figure below gives an overview of the global LAB capacity by region. The Asia Pacific region accounts for nearly half of the global capacity. North America and West Europe have reduced in recent years as rationalization has occurred for the major players. Further details are given in the report.

Global LAB Capacity by Region, 2007
(3.356 million tons)



Strategic issues – threats from inter-material competition and substitution – are discussed, as well as the LAB Value chain.

Some understanding of the value of surfactants for formulators such as Unilever and Procter & Gamble is supplied together with an overview of product substitution issues and new alternatives such as Gas to Liquids (GTL) feedstocks and their potential impact on *n*-paraffin supplies.



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