PETROCHEMICALS

in Nontechnical Language Fourth Edition

CONTENTS

FOREWORD

The energy industry is a complicated technical business. The general public has little understanding of it even though it has an overwhelming impact on our daily lives, whether driving to work or just watching TV. More often than not, the carbon side of this industry has a dark cloud hanging over it in the public eye, largely due to lack of education. Easy-to-read, comprehensible books like this one are a vital part of this educational process.

This naiveté is not just with the way primary energy sources, including renewables, transform into transportation fuels, heating fuels, and electricity. If you ask the typical man on the street where plastics or even detergents come from, he will likely stutter for an answer, not knowing about the petrochemical business. The man on the street is not the only one short on these details. Even those people directly in the oil and gas business have a lack of understanding of this final leg of the hydrocarbon value chain and all its derivative products that make this world a better place to live.

For most of my Shell career, I can put myself in this camp with positions in areas other than petrochemicals. When a job opportunity in Shell's chemical business did come my way, it was critical to ramp up fast on the fundamentals of this complex business. Fortunately, I knew Bill Leffler well and that he had coauthored this book on *Petrochemicals in Nontechnical Language*. Bill has always been a genius in taking difficult concepts and translating them into understandable language even for the nontechnical people like me. I have to admit that tackling all the chemical formulas was not something I was looking forward to doing. But Bill and coauthor Don Burdick did a terrific job in making it all understandable for me in getting to the essence of what is important and how it all works. The book was absolutely invaluable to me.

Over its almost 20-year life, *Petrochemicals in Nontechnical Language* has become a real classic of the PennWell series of books. It is not just because of its readability, which you will deeply appreciate. And it's not just because it quickly allows you to flow through the petrochemical's value chain. Bill and Don have kept it current. This fourth edition brings the material into the 21st century from all aspects.

Since my initial reading, I have continued to use the book as a handy reference. Being an author, I can tell you it is a real accomplishment for Bill and Don to have written the book in a way that is easy to use while rich in content so that you come back to it time and again. I have really enjoyed reading this latest edition, refreshing my learning while adding new insights. The quality of the book is not surprising given the expertise of the authors. Both are educators, writers, and PhDs. Don has more than 40 years of chemical industry experience, including his vice president of marketing role with Haltermann Custom Processing. With an equal amount of time devoted to this energy industry, Bill is a true energy expert across the oil and gas spectrum with his many key roles in Shell. This is just one of five nontechnical books that Bill has authored or coauthored covering upstream, pipelines, and refining.

So whether you are currently in the petrochemicals business, in other parts of the energy value chain, or just the inquisitive common man or woman on the street, this book is well worth your reading. It was Will Rogers who said, "There is nothing so stupid as an educated man, if you get him off the thing he was educated in." Here is a quick way to avoid being stupid about the petrochemicals business.

Lane E. Sloan
Shell Chemical Company President (retired)
Co-author with Christopher Ross of
Terra Incognita: A Navigation Aid for Energy Leaders

PREFACE

"But now ask the beasts, and they shall teach thee."

Job 12:7

We have updated, edited, and rewritten every chapter in this book and even added seven more, qualifying us to use the advertisers' mantra, "New and Improved." With the third edition 10 years in the market place, the need to create a fourth came to us like a paper cut from licking an envelope. We were rereading parts of former editions and noted we said that a big market for polyvinyl chloride was phonograph records. Later on we said, "Probably all the 'wood' on the front of your console TV is polystyrene." Well, lifestyles change with time and so do technologies, stimulating us to produce a new, more useful edition.

After you buy this book, you can use it in at least five ways (besides unabashedly displaying it on your office bookshelf):

- Read it cover to cover for a nontechnical education covering 90% (by volume) of the traded petrochemicals.
- Read a chapter or section as subjects come up in your business life. Each chapter is designed to be a self-contained description of one petrochemical. If you're too busy, there are short summaries at the end of each chapter.
- Use it as a nontechnical encyclopedia. The glossary in the back has more than 300 technical terms and is blessedly nontechnical. And if you can't find what you need in the index at the very end of the book, you should have gone to engineering school because you now have a job where you're in over your head.
- Use it as a primer in petrochemical economics. Many of the chapters have material balances that will let you put current prices to them.

- Recommend it to your team members, team leaders, or anyone else who needs to know at least half as much about petrochemicals as you do.

There are four parts to this book, if you leave out the housekeeping and appendices. The first is only two chapters—the mandatory discussion of chemistry and a primer on processes in general. Our editors tell us the book would not be technically complete without them. It's not bad, but we met a reader once who just skimmed it and did okay with the rest.

The next five chapters cover the base chemicals—the building blocks benzene, toluene, xylene, ethylene, propylene, and the C_4s—from which most of the remaining petrochemicals are derived.

The third part, a large midsection of 17 chapters, has all the first and second line derivatives. Some of them will be of interest to you. Some will not.

The final section covers polymers, which are "borderline" petrochemicals. We debated whether they belong in a book about petrochemicals, but most of the clients to whom we give the course based on this book want to know about them. So we wrote them and they seemed to complete the linkage from raw materials (coal, oil, gas) all the way to consumer products. If you don't agree, don't read them.

At the end of the text are the quick references, the glossary and the index. Use them when you have little time for pedantic endeavor.

As a side note about nomenclature in this book, we should mention that we switch back and forth indiscriminately among synonyms, notations, and different conventions. For example, we use butylene sometimes and butene others; C_2H_4 sometimes, $CH_2{=}CH_2$ others. That's the way it is in industry, so you might as well get used to it here.

D. L. B.
W. L. L.

Bonds. The connections between atoms in figure 1–1, shown as straight lines, are in fact electrical connections, only shown in illustrations as dashes. Each dash or bond contributes one to satisfying the valence.

Paraffins

More complex *molecules* (combinations of carbon and hydrogen atoms bonded together) can make a seemingly endless number of combinations. In figure 1–2, the next simplest molecule has two carbons connected to each other and to three hydrogen atoms each to satisfy the valence of four. Similarly, adding carbons and hydrogens to the chain gives propane (C_3H_8), normal butane (C_4H_{10}), and normal pentane (C_5H_{12}). Chemists call this family of organic compounds the *alkanes* and occasionally *saturated hydrocarbons.* Others use the word *paraffins.* (In everyday, nontechnical use, *paraffin* refers to wax, which is, in fact, a mixture of $C_{30}H_{62}$ to about $C_{50}H_{102}$. Note that the general formula for paraffins is C_nH_{2n+2}.)

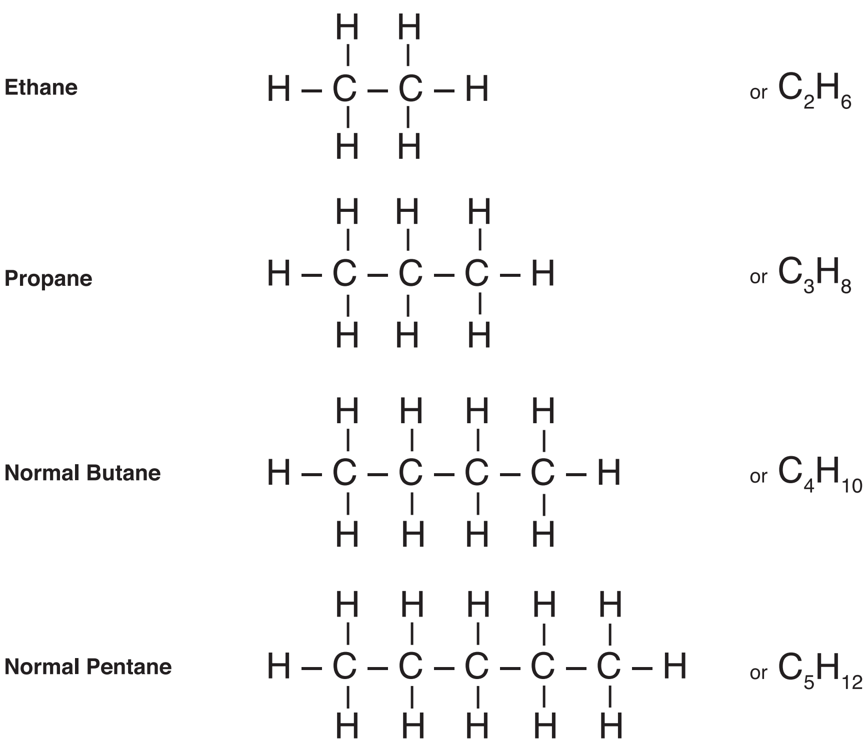

Fig. 1–2. Alkanes or paraffins

Kekulé's theory using quantum mechanics. There are still some loose ends, but no good alternate theory has turned up yet.

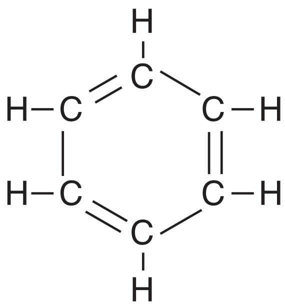

Fig. 3–1. Benzene

Benzene had limited commercial value during the 19th century. It was used primarily as a solvent. In the next century, gasoline blenders discovered benzene had good gasoline octane characteristics. As a consequence, there emerged an incentive to recover all the by-product benzene that was produced in the coke ovens at steel mills. Starting around World War II, chemical uses for benzene began, primarily in the manufacture of explosives. Coke oven benzene was diverted from gasoline blending to the chemical industry. Furthermore, by midcentury, the petrochemicals industry was bidding away benzene from the refining industry to keep up with rapid growth in nylon, styrene, and other applications. The largest user of benzene ultimately turned into the largest supplier.

The increasing demands for benzene by the petrochemicals industry led to new and improved manufacturing processes—catalytic reforming, toluene hydrodealkylation, and toluene disproportionation, the last two being ways to turn toluene into benzene. Toluene goes in and out of commercial vogue, and the markets for gasoline (a toluene user) and benzene (for styrene, nylon, etc.) move in different cycles. A fortuitous source of benzene emerged in the 1970s when olefin plants began using naphtha and later heavy gas oil as feedstocks and produced by-product benzene.

Even more incentive to remove benzene from gasoline started in the last decades of the 20th century. Environmental regulators around the world responded to the conclusive evidence that benzene was a carcinogen, even in the trace amounts present in gasoline vapors that escaped from gasoline storage tanks and leaky car tanks. Regulators have repeatedly lowered the allowed benzene content in gasoline, prompting the construction of additional extraction units to remove the benzene from gasoline before it was shipped.

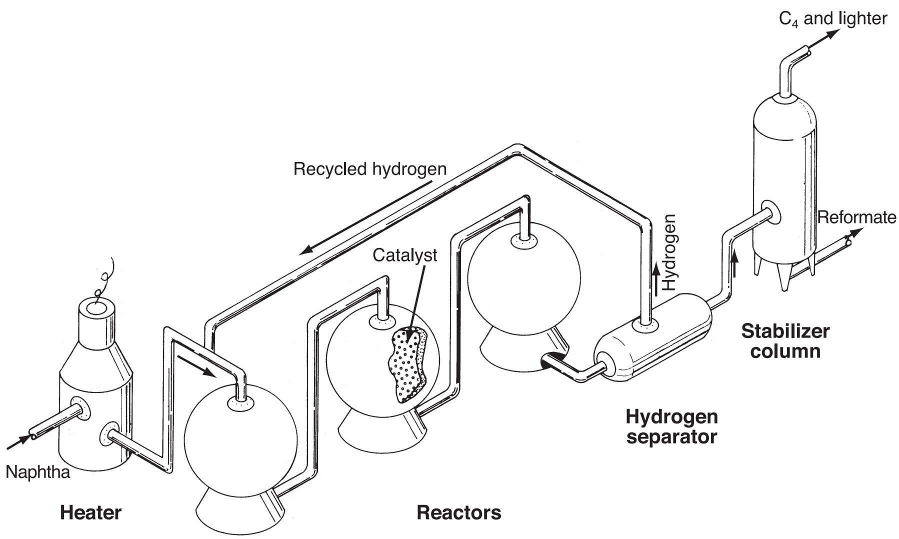

Fig. 3–4. Semicontinuous cat reformer

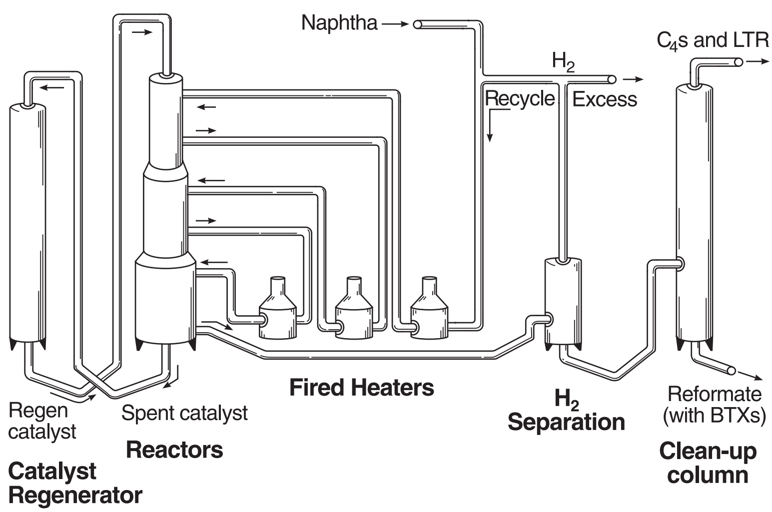

Fig. 3–5. Continuous cat reformer

Propylene

Propylene is also a colorless gas at room temperature. It is just as flammable as LPG and can be used as a supplement or substitute for LPG. It does, however tend to form gums in the valves and so is not widely used this way. Besides, the petrochemicals industry pays a higher price for propylene than LPG users are willing to pay.

Propylene is traded commercially in three grades: refinery, chemical, and polymer grade. The difference is almost entirely the ratio of propane to propylene in the stream. Refinery grade, which comes from refinery cat crackers and cokers, usually runs about 50%–60% propylene; chemical grade, which comes from heavy liquids crackers, runs 90%–95% propylene; polymer grade is at least 99% propylene. Upgrading refinery grade and chemical grade is just a matter of fractionation, which several merchant processors will readily do for a fee (fig. 5–10).

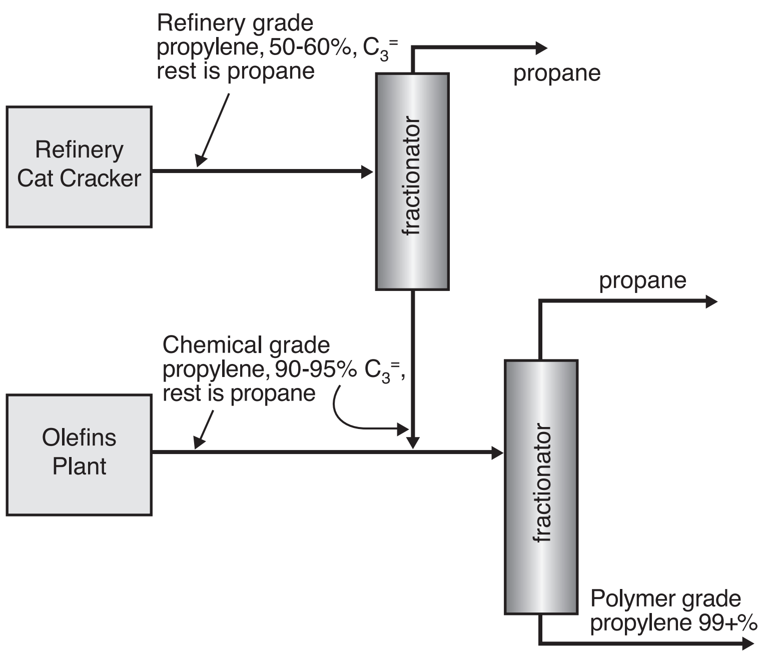

Fig. 5–10. Grades of propylene

Most propylene applications can use chemical grade, but most polypropylene processes require high purity, polymer grade.

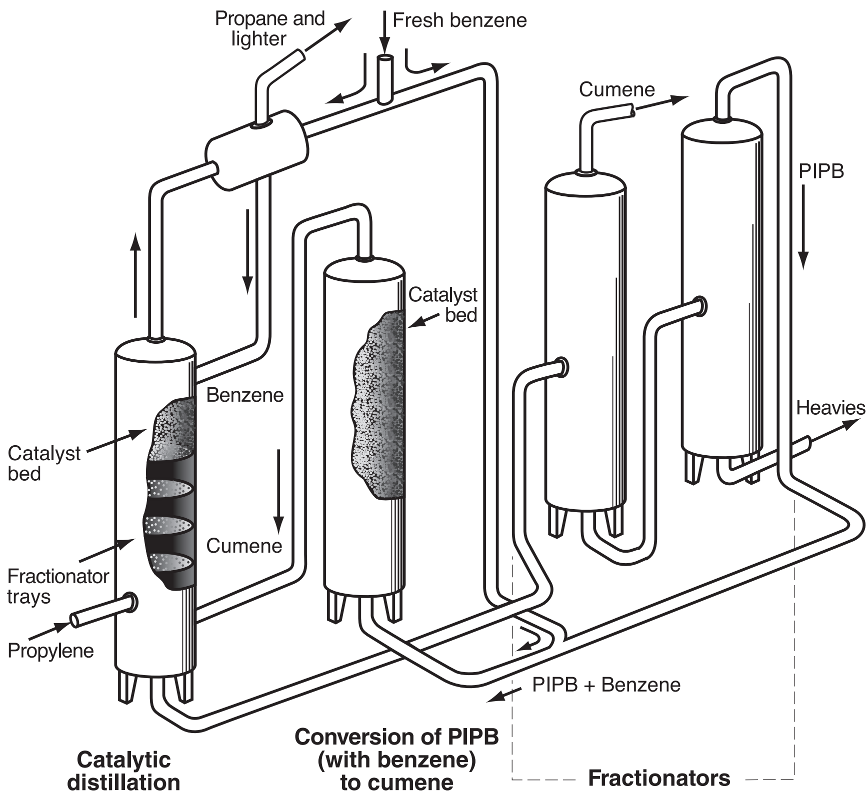

Fig. 8–3. Cumene by catalytic distillation

Chemical grade propylene is introduced to the middle section of the column as a vapor and will rise up through the catalyst bed at the top of the column. Benzene is introduced at the top of the column as a liquid and trickles down through the catalyst bed, mixing in countercurrent flow with the propylene vapors. Zeolite-based catalysts cause the direct alkylation of benzene with propylene, forming cumene. (As explained previously, alkylation is the addition of an alkyl group to another organic compound.) One of the side reactions also produces an appreciable amount of polyisopropyl benzene (PIPB) that will have to be dealt with in the other reactor in figure 8–3.

Both the cumene and the PIPB will continue down the column. The hot propylene and cumene vapors and the column trays will strip any remaining unreacted benzene from the falling cumene/PIPB liquids. The unreacted benzene will be pushed up the column and back to the catalyst bed, where it will react with the propylene.

Chapter 10 in a nutshell…

Ethylene dichloride is made mostly so that vinyl chloride can be made from it. There are two routes. The direct route involves reacting ethylene with chlorine. The indirect route is integrated with the vinyl chloride plant, which uses ethylene and vinyl chloride as the basic feedstock. Dehydrogenation of EDC produces vinyl chloride and hydrogen chloride. The HCl is subsequently reacted with ethylene and oxygen to produce EDC.

Epichlorohydrin, made from propylene and chlorine and from glycerine and HCl, is primarily used to make epoxy resins.