Ultraclean Transportation Fuels
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Foreword

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Before agreeing to publish a book, the proposed table of contents is reviewed for appropriate and comprehensive coverage and for interest to the audience. Some papers may be excluded to better focus the book; others may be added to provide comprehensiveness. When appropriate, overview or introductory chapters are added. Drafts of chapters are peer-reviewed prior to final acceptance or rejection, and manuscripts are prepared in camera-ready format.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previously published papers are not accepted.

ACS Books Department
Preface

Transportation fuels account for a significant portion of crude oil consumed in the United States. Hence, the importance of clean transportation fuels in the nation’s economic development, environmental and public health improvement cannot be overly emphasized. Of the total manmade air emissions in the United States, highway transportation is responsible for 57% of the carbon monoxide, 30% of the nitrogen oxides, and 27% of the volatile organic compounds emissions. Driven by the continuing desire of the public for personal mobility, dramatic increases in vehicle numbers and miles have been forecasted. This growth will lead to poorer air quality unless ultraclean transportation fuels are developed and deployed.

To address air pollution problems, the U.S. Environmental Protection Agency (EPA) proposed and developed new vehicle emissions standards. Ultralow sulfur standards for diesel fuel began in 2006. Gasoline sulfur standards have been phased-in since 2004. The EPA Tier 2 tailpipe emissions regulations for light duty vehicles have already taken effect. Standards have also been developed for heavy-duty vehicles that would be phased in from 2007 to 2010.

During the next several years, the United States will implement new, stricter Federal and state emission standards for highway vehicles; encounter more volatile global energy markets; face increased cost of technologies for clean transportation vehicle and fuels production; and encounter increased threat of global climate change. Therefore, it is essential to aggressively pursue the research and development of advanced technologies for high efficiency, low-emissions highway vehicles, as well as for the production of ultraclean fuels required for their operation.

The Department of Energy (DOE) utilized the unique scientific capabilities of its national laboratories and partnering with industry to identify, study, and develop advanced fuels for tomorrow’s vehicles. Through these efforts, an Ultraclean Transportation Fuels (UCTF) Program was initiated at the beginning of this century.
The DOE UCTF Program was designed to promote partnerships with industry as well as to develop, demonstrate, and deploy technologies and systems to ensure that the nation's future transportation fuels, utilized in advanced highway vehicles, will contribute to dramatically improved environmental quality, energy security, and economic competitiveness. This new generation of advanced fuels will achieve decreases in air pollution, while increasing or maintaining vehicle performance.

In recent years, research and development activities on ultra clean transportation fuels have significantly increased to meet the increasingly demand for clean fuels that will meet the strict environmental regulations.

This book is the result of two symposia on ultraclean transportation fuels presented at the 2001 and 2005 Fall National Meetings of the American Chemical Society. Nineteen papers were presented in three sessions at the 2001 Meeting and fifteen papers were presented at the 2005 Meeting in two sessions. For a more comprehensive product, authors of papers presented at both National Meetings were invited to submit manuscripts for consideration for publication in the book. The manuscripts were peer reviewed.

This symposium series book describes the recent advances in various aspects (production, processing, upgrading, and utilization) of such recent research and development efforts related to ultraclean transportation fuels from a variety of hydrocarbon feedstocks (coal, petroleum coke, biomass, waste oil, and natural gas).

The form of this book is organized in the following six parts:

- general overview
- basic fundamental and applied research of production from various feed-stocks
- novel methods of upgrading for meeting strict environmental standards and fuel specifications
- utilization in environmentally sound ways
- advances in development of new catalysts for more efficient and cost-effective processes
- computational fluid dynamics modeling to enhance reactor design and optimize transportation fuels reactors.
The authors of each chapter are sharing their timely research and their expert insights in this book. The diversity of their experiences is taking the ultraclean transportation fuels advancement forward.

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Chapter 1

Overview of Fundamentals of Synthetic Ultraclean Transportation Fuel Production

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With ever increasing requirements for clean transportation fuels and liquid hydrocarbon supplies, there is an opportunity to produce significant quantities of synthetic ultra-clean fuels that are essentially sulfur-free. These synthetic fuels can be produced from natural gas, coal, petroleum coke, biomass, and other non-traditional hydrocarbon sources. Most of these products are fungible and compatible with current products and distribution infrastructure and can be produced at costs competitive with conventional crude oil-derived products under certain market conditions.

Introduction

Currently, petroleum-derived products meet the majority of the world’s transportation fuel needs. However, with rising prices and concern over the amount of conventional oil remaining in the world, there is growing interest in producing transportation fuels from alternative energy sources, such as natural gas, coal, petroleum coke, and biomass. Production of synthetic ultra-clean transportation fuels from these diverse feedstocks can supplement world fuel supplies, mitigating our dependence on traditional crude oil for fuels. In addition, these synthetic products are exceptionally low in sulfur and other undesirable components, meeting or exceeding all proposed standards for clean fuels. Ultra-clean synthetic fuels of interest include Fischer-Tropsch liquids, methanol, dimethyl ether and hydrogen.

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Production of synthetic liquid fuels has a long history with significant advances being made since the initial use of the processes. In the 1920s, two German scientists working at the Kaiser Wilhelm Institute, Franz Fischer and Hans Tropsch, passed coal-derived synthesis gas over metallic catalysts and produced pure hydrocarbons. The Fischer-Tropsch (F-T) process, invented in petroleum-poor Germany, was used by Germany during World War II to produce alternative fuels. Production reached more than 124,000 barrels per day (b/d) in 1944 (1).

This process was first used commercially in the 1950s by the South African Synthetic Oil Corporation (Sasol) to produce transportation fuels (gasoline and diesel) using synthesis gas produced by the gasification of coal. The objective was to convert low-grade coal into petroleum products and chemical feedstocks (2). Today, Sasol produces the equivalent of 150,000 barrels per day of fuels and petrochemicals from coal via its indirect liquefaction process.

The Fischer-Tropsch process is the most notable of the various synthetic fuel processes and has products that range from lighter hydrocarbon liquids like naphtha to diesel fuel and heavier hydrocarbons like lubes and waxes. The final product mix is dependent upon operating conditions and process units, such as inclusion of hydrocracking functionality. By varying the design and operating conditions in the reaction section, the plant can optimize production of the desired product slate (3).

Using non-traditional feedstocks to produce synthetic ultra-clean fuels, including F-T liquids, methanol, dimethyl ether, and hydrogen has numerous benefits including (4):

- Expansion of liquid fuel supply.
- Reduction of U.S. dependency on imported oil.
- Enabling of exhaust aftertreatment systems to be used on gasoline and diesel engines that will significantly reduce emissions of nitrogen oxides, carbon monoxide, hydrocarbons, and particulates.
- Production of a sequestration-ready stream of carbon dioxide, thus enabling potential reductions of greenhouse gas emissions.
- Production of fuel which could help reduce world oil price.

Production of Synthetic Ultra-Clean Fuels

Synthetic ultra-clean fuels are produced from simple chemical building blocks derived from the breakdown of natural gas, coal, petroleum coke, or biomass. Unlike traditional fuel products, which naturally have substantial impurities such as sulfur and aromatic material which must be removed, the synthetic fuels are produced by building up from molecules which are free of...
impurities. Therefore, the resultant products are essentially pure, requiring minimal or no further treatment.

The production of ultra-clean synthetic fuels from various feedstocks can be thought of as a three-step process. First, synthesis gas (syngas) is produced from the hydrocarbon feed. Second, the syngas, primarily a mixture of carbon monoxide (CO) and hydrogen (H₂), can be further processed through a chemical combination and conversion process to manufacture a heavier liquid hydrocarbon and the desired fuel. The most notable is the F-T process, but other processes also exist. Alternatively, if the desired product is hydrogen, the second step is a shift reaction to convert the carbon monoxide to additional hydrogen and carbon dioxide by adding steam. Finally, the desired products must be separated and purified as necessary to meet specifications and to move the products to consumer markets.

Syngas Production

There are various feedstocks and chemical conversion reaction schemes that can be used to produce synthetic ultra-clean fuels. All start with the production of syngas, a hydrogen/carbon monoxide mixture.

Syngas From Heavy Hydrocarbons

When starting with coal, petroleum coke, biomass or other heavy solid hydrocarbons, the feedstock is gasified by mixing it with oxygen or air in the presence of steam which partially oxidizes the carbon in the feedstock to produce a mixture of CO, H₂, and small amounts of other chemicals. The amount of air or oxygen used during gasification is carefully controlled to be less than stoichiometric quantities so that complete combustion does not occur and only a relatively small portion of the fuel burns completely. The reactions take place at high temperatures (1,000°C or more), which is a result of the exothermic combustion reactions (Reactions 1 to 3) required to drive the endothermic reduction reactions (Reactions 4 and 5). Carbon dioxide (CO₂), sulfur, nitrogenous compounds, and other impurities are generally present, which must be subsequently removed from the gaseous stream before further processing.

Oxidation (2):

\[
\begin{align*}
C + \frac{1}{2}O_2 &\rightarrow CO \\ C + O_2 &\rightarrow CO_2
\end{align*}
\]

\[\Delta H = -123 \text{ kJ/mol}\] (1)
\[\Delta H = -406 \text{ kJ/mol}\] (2)