MEMBRANES IN SEPARATIONS: COMMERCIAL ADVANCES IN REFINERY, PETROCHEMICAL/CHEMICAL AND INDUSTRIAL GASES APPLICATIONS

MULTI-CLIENT STUDY PRESENTATION

(study completed November 2016)

TCGR THE CATALYST GROUP RESOURCES™

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MEMBRANES IN SEPARATIONS: COMMERCIAL ADVANCES IN REFINERY, PETROCHEMICAL/CHEMICAL AND INDUSTRIAL GASES APPLICATIONS

STUDY COMPLETED NOVEMBER 2016!

There are few things better than having the industry's leading industrial organizations and experts help to shape the scope and content of a technical and strategic study of such importance. Yet, The Catalyst Group Resources (TCGR) has benefitted from such insight for its recently completed, cutting-edge study addressing membranes in separations applications. **In their role as "charter" subscribers, these international membrane developers/producers and end users across applications including gas separations (NG, CO_2, H_2, N_2, olefin/paraffin, etc.) and liquid separations (e.g., refinery streams, aromatics, lube oil, solvent dehydration, wastewater, etc.) have all provided their prioritized inputs into the topics addressed, the areas emphasized, and the focal points for opportunity assessment.** The improved and expanded Table of Contents from the completed study is now depicted beginning on page 12 for consideration by new subscribers.

I. ABSTRACT & EXECUTIVE SUMMARY

More so than ever, the need to reduce energy usage and costs in the production and purification of gas and liquid streams in refining, petrochemical/chemical and industrial gases applications is paramount. Whereas older technologies including distillation and ab/adsorption are well-proven, they are expensive and energy-intensive. As a result, numerous and significant advances have led to alternatives in application-specific membranes which are more technologically and commercially viable. In addition, the companies funding/conducting the RD&D increasingly include major end users, so implementation is taking place more broadly and at larger scales of operation. It is an opportune time for industry participants to assess the progress, evaluate opportunities and consider the competitive implications on their operations and strategies going forward.

This study from TCGR, entitled "**Membranes in Separations: Commercial Advances in Refinery, Petrochemical/Chemical and Industrial Gases Applications,"** documents and assesses, on both scientific and techno-economic bases, recent developments in membrane technologies and compares them to current industrial state-of-the-art alternatives (e.g., distillation, ab/adsorption, cryogenics) with the objective of providing insightful, timely advice in both R&D/technical and commercial directions.

Among the critical findings captured in the study are:

- There are numerous short term (<5 years) opportunities for membranes, notably in retrofitting in H_2 management within refineries, reformers, ethylene (polymer and crackers) and ammonia plants to improve energy efficiency/off-gases management and in CO_2 natural gas (and shale gas) purification removal systems; in the medium term (5+ years) the emergence of olefin/paraffin separation systems will open a major new application market and in the longer term (10+ years) CO_2 flue gas capture for the power, petrochemical, cement and steel industries, to improve on GHG management will provide future opportunity.
- Membrane systems represent a specialty, high growth industry, but one characterized by very specific applications/technology requirements; competitors have developed into sub-market groupings who, as they grow and consolidate, will become larger companies able to serve broader industry segments, a trend worth noting.

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- Increasingly, membrane systems are becoming the choice for retrofit applications, where skid mounted units can expand capacity, or improve product yield and quality at a fraction of the CAPEX costs of added new units, or expanding additional reactor capacities.

- A key challenge membranes face is their cost/performance relative to incumbent process solutions, particularly in terms of scale; a positive is that, depending on the application for smaller plant solutions or retrofit to incrementally expand or improve operations, membrane systems have a significant advantage, because they can be deployed within the existing process CAPEX without significant infrastructure costs.

- Although in its infancy (in pilot plant demonstration) as an application, olefin/paraffin separations represent a huge untapped application which in the longer term (5-10 years) could vastly expand the membrane industry; on the lower growth end, the well-established smaller plant N_2 separations segment is slower growth and moving toward market saturation, contrasted by the H_2 process recovery market and site management which has significant expansion potential.

- Among the largest regional growth areas over the next 5-10 years are the Asia/Pacific and China, both in water/wastewater and in plant retrofit for membrane systems in the refining and petrochemical/chemical industries.

A snapshot of the market characteristics for membranes in separations is depicted in the Table below:

Market Segment	Membrane Market Share	Growth in Market	Pace of R&D
Gas Separation			
Nitrogen from Air	◑	↑	↑↑
Oxygen from Air	◔	↑↑↑	↑↑↑
Hydrogen			
H_2/Gas (CO, N_2, C_1, C_2)	◔	↑↑	↑
H_2/gas (C_3+, CO_2)	◔	↑↑↑	↑
Natural Gas			
CO_2 Removal	◔	↑↑	↑↑↑
NGL Removal and Recovery	◔	↑↑	↑↑
N_2 Removal and Dehydration	◔	↑↑	↑↑
Vapor (C_2+)/Gas	◔	↑↑↑	↑↑↑
Vapor/Vapor (Olefin/Paraffin)	◔	↑↑↑	↑↑↑
CO_2 (flue gas)	◔	↑↑	↑↑
CO_2 (biogas)	◕	↑↑↑	↑↑↑
Liquid Separation			
Lube Oil Processing	◔	↑	↑
Solvent Dehydration	◔	↑	↑↑↑
Wastewater Purification	◔	↑↑	↑↑

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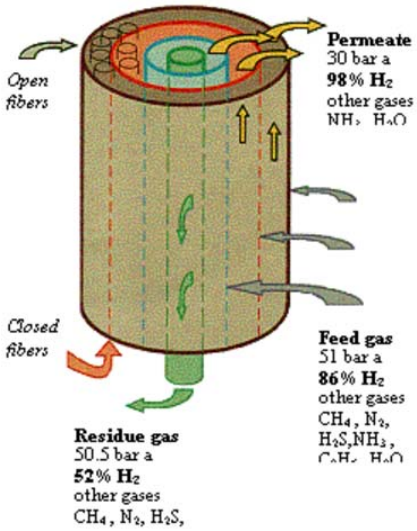
II. BACKGROUND

At their foundation, membrane processes have significant advantages over alternatives. Relative to adsorption, they do not require material regeneration. They also require less energy and space compared to conventional distillation processes. As an example, hydrogen (H_2) production has attracted a lot of attention due the number of applications in the energy sector, including its potential role in the "next generation" of clean energy technology. Nearly 80% of hydrogen production is achieved from steam methane reforming (SMR) and is currently considered the least expensive method for hydrogen production. Despite this, significant drawbacks exist due to the high temperatures (900-1100 °C) and thermodynamics of the reaction. A number of companies are working on the development of **dense metal membranes** to significantly decrease energy costs while maintaining hydrogen yield and selectivity.

An addition to SMR is the water gas shift (WGS) reaction which is exothermic and as a result the conventional process requires a high-temperature shift followed by a low-temperature shift process. The WGS reaction is considered a continuum of the SMR reaction, reforming the carbon monoxide produced from the SMR with water to produce hydrogen. In this case, the application of **hollow fiber type membranes** have resulted in increases in separations efficiencies and decreases in separation energy reductions of both in the range of 25%.

In refineries, the hydrodesulfurization (HDS) reaction takes place in a fixed-bed reactor at elevated temperatures and elevated pressures in the presence of a nickel or cobalt based catalyst supported on alumina. Membranes such as Air Liquide MEDAL™ have also been successfully employed in refinery gas separations for ultra-low sulfur diesels (see Figure 1). The technology uses the **selective membrane** for hydrogen recovery and recycling at 350 °C. As the conventional process operates at 900 °C significant energy savings can be realized.

Figure 1: Air Liquide's MEDAL™



Source: Air Liquide at http://www.medal.airliquide.com/en/hydrogen-membrane-gas-separation/hydrogen-membrane-refineries.html

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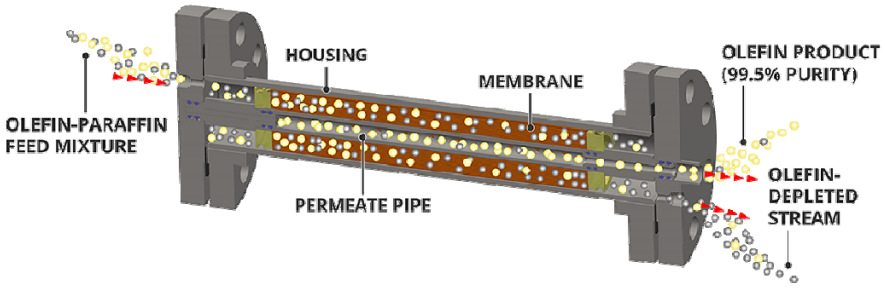
In petrochemical production, including aromatics and olefins, the area of olefin-paraffin separation from paraffin is another application of membranes replacing the alternative. Traditionally, cryogenic distillation units are often employed, even if these processes are energy- and cost-intensive, mainly caused by the refrigeration of each mixture. **Polymer membranes** have been evaluated in olefin-paraffin separations. The incorporation of transition metals, such as silver or copper to the membrane matrix allows permeability of the olefin through the membrane by the formation of a metal-olefin complex. These reactions are exothermic which indicate that the equilibrium tend to shift to reverse reaction with the temperature. Thus through controlling the temperature and pressure, i.e. temperature and pressure swings, the separation process can be achieved. This has been particularly successful in the separation of C_2 and C_3 olefin-paraffin mixtures, with energy savings in the region of 30-90% documented.

In a specific example, Imtex Membranes Corp. has developed a membrane separation process that has shown performance stability over extended periods of operation during trials using spiral wound membrane elements (see Figure 2). Imtex has continued to optimize the hydrogel-based membrane process, and through a significant technology advancement, has demonstrated continuous, uninterrupted operation in olefin/paraffin gas separation. The performance stability of the Imtex membrane stands in contrast to dry solid polymeric and immobilized liquid membrane technologies for which stability, permeation rate and selectivity challenges have been well documented. Results have been encouraging for C_2, C_3 and C_4 splitting applications as greater than 99.5% olefin purity was achieved in all cases with steady permeation at commercially viable rates. With these characteristics and its modular nature, Imtex membrane technology is presented as a practical alternative to the costly distillation approach (Imtex, 2015).

Figure 2: Imtex Permylene™ Membrane



Source: Imtex, 2015

In gas separation/processing**,** Evonik Industries is expanding its promising membrane business. To this end, the specialty chemicals company will further expand its Austrian site in Lenzing/Schörfling to double the existing production capacities for the hollow-fiber membrane modules of its SEPURAN® brand. The new hollow fiber spinning plant will be dedicated to the production of membrane modules for efficient gas separation particularly for nitrogen extraction. The SEPURAN® membrane offers a particularly efficient method for the separation of gases from gas mixtures such as methane, nitrogen, or hydrogen. Evonik is investing an amount in the mid double-digit million € range in the plant and its infrastructure. The production of additional membrane modules is projected to begin in late 2017 (Evonik, 3/3/2016).

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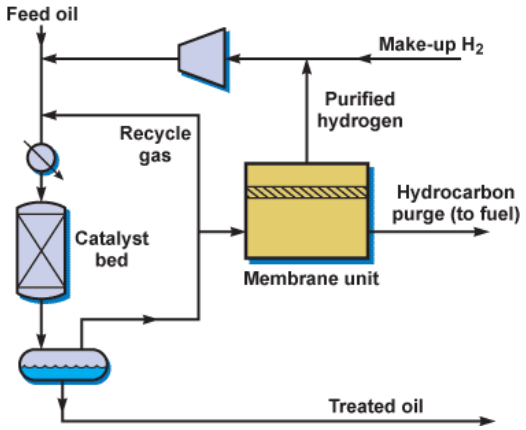
Other application areas/examples for membranes in separations applications are also worthy of note, including:

Refining Applications

- According to MTR, VaporSep-H2™ offers a method for recovering hydrogen from refinery streams wherein hydrogen permeates preferentially through the membrane, producing a purified hydrogen "permeate" stream and a hydrocarbon-enriched "residue" stream (see Figure 3). The available pressure for the purified hydrogen depends on the feed conditions, but can be as high as 1500 psi. The hydrocarbon-enriched "residue" is recovered at close to the feed pressure, and can be sent to directly to fuel, or first treated for liquefied petroleum gas (LPG) recovery if these components have value (MTR).

Figure 3: VaporSep-H2™ Solution



Source: MTR

Petrochemical/Chemical Applications

- In a recent advancement, Compact Membrane Systems (CMS), an industrial membrane manufacturer in Newport, DE (USA) announced plans to install a pilot system at the Delaware City Refinery of PBF Energy for testing newly-developed membranes that effectively separate olefins from paraffins. Using a perfluoropolymer material, CMS has developed high performance, long-lasting membranes that provide high purity streams of olefins to the end user. Unlike previous attempts to develop membranes for this purpose, the CMS material has been shown to last >300 days in laboratory tests and is resistant to poisons such as acetylene, hydrogen and hydrogen sulfide. The pilot demonstration at the PBF refinery will be the first on-site test of the material. (Compact Membrane Systems).

- Dow Global Technologies, LLC, disclosed in a U.S. patent application the use of a hollow fiber molecular sieve membrane as a low-cost and low-energy alternative to cryogenic processes to separate olefins and paraffins in a gas stream from a steam cracker. The membranes are formed from the pyrolysis of aromatic polyimide precursors, such as 6FDA/BPDA-DAM, or MATRIMID™ (Membrane Quarterly, 12/2015, Vol. 30, No. 4, p. 18).

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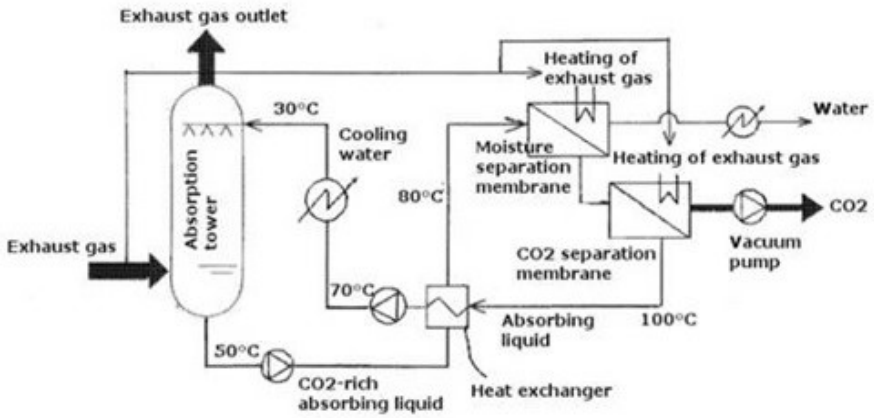
- In the application area of combined isomerization and separation, recent experiments have demonstrated much higher production and yield. The equilibrium composition limitation imposed on conventional fixed bed reactors (FBRs) can be overcome, reaching p-xylene yields beyond equilibrium. An increase in p-xylene yield in catalytic membrane reactors (CMRs) as high as 26% compared to FBR was achieved at 643°K. ExxonMobil has been granted a patent for a xylenes isomerization process using a zeolite CMR (Petroleum Technology Quarterly, Q1/2015, p. 111).

Industrial Gas Applications

- Hitachi Zosen has developed a combined membrane separation/absorption process to recover CO_2 from flue gas exhaust, as captured in published U.S. patent application 2015/0147252 (see Figure 4). In this approach, the energy consumption needed to perform the separation is a key consideration. The amine regeneration step usually requires heating to about 100-130°C, but using a membrane to remove CO2 from the spent amine solution pushes equilibrium to a point where less heat is required for regeneration, so significant energy savings are achieved (Membrane Quarterly, Vol. 30, Number 3, 9/2015).

Figure 4: Hitachi Zosen's Hybrid Absorption/Membrane Process



Source: Membrane Quarterly, Vol. 30, Number 3, 9/2015

III. THE NEED FOR THE STUDY

Beyond raw material costs, the cost of energy is the most important factor in the refining, petrochemical/chemical and industrial gases industries producing large volumes of fuels and bulk/intermediate chemicals. As many refiners, petrochemical/chemical and gas producers face an increasing global competitiveness, the search for opportunities to reduce production costs without negatively affecting product yield or quality is imperative.

Uncertain crude oil and energy prices in today's market place can negatively affect predictable earnings. Improving energy efficiency via improved separation/purification processes increases the bottom line of manufacturing plants. In order to remain competitive in production costs, as well as to take advantage of leading-edge technologies providing product/process capabilities which distinguish them from their competitors, refiners and petrochemical/chemical producers, as well as those supplying industrial gases, must consider the alternatives to current practices.

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This TCGR study addresses the development, implementation and implications of membranes in separations with an emphasis on the resulting product/process improvements affecting costs, purity and functionality of the products. These include energy efficiency gains, waste/by-product minimization, and product performance improvement/differentiation. The study documents the incumbent technologies and the market sizes/growth rates for their applications. It provides an assessment of the technology and product suppliers and highlights strengths/weaknesses relative to the new membrane-based offerings. It then indicates the opportunities for advancement and the challenges which remain, notably regarding membrane stability and re-use. The competitive and strategic implications of the advances in membranes, including the timing of their commercial implementation and impacts on the developers/partners, are assessed.

For those that understand and appreciate this study undertaking, you will know how important and critically timely this evaluation is! With energy/production costs playing a critical role in competitiveness, and product performance/capabilities defining differentiation between players, the next several years are certain to be telling. Thus, TCGR's study - a technical and commercial assessment - is warranted.

This new study, completed in November 2016, "**Membranes in Separations: Commercial Advances in Refinery, Petrochemical/Chemical and Industrial Gases Applications,"** complements an ongoing portfolio of similarly well-received TCGR reports delivered to clients over recent years. This growing experience demonstrates TCGR's unique capability, resources, and expertise to deliver exceptional insight.

Recent multi-client reports and limited-client reports include:

- ***The Intelligence Report: Business Shifts in the Global Catalytic Process Industries, 2015-2021*** (May 2016)
- ***The Middle-East Catalyst Market: Technologies, Applications and Opportunities*** (March 2016)
- ***The Asia-Pacific Catalyst Industry: Markets, Technologies and Manufacturers*** (September 2015)
- ***Specialty Zeolites in Catalysis, 2002-2020: International, Commercial and Technical Progress – A New Era!*** (March 2014)
- ***The Catalytic Process Industries in China: Markets, Technologies & Strategic Implications*** (4 part Series – 2013)
- ***The Industrial Adsorbents Business: Commercial Strategy, Technical and R&D Assessment in Refining, Chemicals/Syngas, Natural Gas and Industrial Gases*** (July 2013)
- ***FCC Additives: Meeting Refiners' Environmental, Performance & Product Slate Flexibility Requirements 2013-2018*** (June 2013)
- ***Unconventional Catalytic Olefins Production: Commercial Vision and Breakout?*** (January 2013)

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IV. SCOPE AND METHODOLOGY

TCGR's study documents and assesses, on both scientific and techno-economic bases, recent developments in membrane technologies and compares them to current industrial state-of-the-art alternatives (e.g., distillation, ab/adsorption, cryogenics) with the objective of providing insightful, timely advice in both R&D/technical and commercial directions.

Topics included are:

- Market size/growth, including commercialization status
- Applications in gas, liquid and reactive separations
- Advances by membrane type, developer
- Strategic analysis and competitive implications

As depicted in the study's actual Table of Contents as shown beginning on page 12 (including "charter" subscriber inputs), TCGR's study begins by completing an overview of the market size and growth for membranes by type and application **(Section III)**. An indication of each membrane's commercialization status is provided as well as the prospects and/or timing of future commercialization for those still at the pilot or development scale. The developers of the technology, as well as their partners, are analyzed regarding implications on incumbent technologies and suppliers.

Section IV. Advanced Separations via Membranes, documents the breadth of membrane-based separation applications by type, notably gas separations and liquid separations, highlighting the following (among others): H_2, air, olefin-paraffin, natural gas and refinery/petrochemical streams (e.g., HDS, oxygenates, aromatics, solvent dehydration, lube processing and wastewater treatment). Incumbent technologies, their suppliers and the progress towards commercialization are captured. *It is in this section that the study's "charter" subscribers (i.e., those who signed up prior to study launch) have provided input/guidance regarding the applications, and membrane types, of greatest interest to them.*

Section V. Technological Advances in Membranes for Separations, documents the recent RD&D towards pilot and commercialization across membrane types and applications. These include the following (among others): nonporous, porous, facilitated transport and reactive membranes as well as membrane modules. An indication of technology leaders is provided alongside the relationships between developers and users (e.g., partners) with implications on commercialization progress, timing and likelihood of success.

Section VI. Strategic Analysis and Recommendations, provides an insightful analysis of critical points in commercial and technical developments and opportunities. Issues of commercialization status, competitive landscape, remaining challenges/opportunities and strategies for growth are documented.

All TCGR studies are characterized by competitive and strategic insights for industrial and financial investment companies to evaluate. These include key trends, concerns, conclusions on the best return on investment (ROI) actions, competitive expectations and strategic SWOT's on the players. TCGR is noted for its sound strategic advice in over 30 years of experience.

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TCGR's unique background and established global Dialog Group® ensures expert capability and skill level in this study area. TCGR will utilize numerous deeply experienced experts in membranes and separations to assist us to provide insights beyond what other sources that do not have the reach and industrial experience can provide.

As it does in each of its industrially-focused multi-client studies, TCGR has sought input from "charter" subscribers to help shape the report's final scope/ToC so that it covers and emphasizes the most pertinent content due to the large volume of research and the numerous areas (i.e., membrane type, application area, etc.) that are of interest.

V. QUALIFICATIONS

The Catalyst Group Resources, a member of The Catalyst Group, works with clients to develop sustainable competitive advantage in technology-driven industries such as chemicals, refining, petrochemicals, polymers, specialty/fine chemicals, biotechnology, pharmaceuticals, and environmental protection. We provide concrete proven solutions based on our understanding of how technology impacts business.

Using our in-depth knowledge of molecular structures, process systems, and commercial applications, we offer a unique combination of business solutions and technology skills through a range of client-focused services. Often working as a member of our clients' planning teams, we combine our knowledge of cutting-edge technology with commercial expertise to:

- Define the business and commercial impacts of leading-edge technologies
- Develop technology strategies that support business objectives.
- Assess technology options through strategy development, including:
  - Independent appraisals and valuations of technology/potential
  - Acquisition consulting, planning and due diligence
- Provide leading-edge financial methodology for shareholder value creation
- Lead and/or manage client-sponsored R&D programs targeted through our opportunity identification process.
- Provide leading information and knowledge through:
  - World-class seminars, conferences and courses
  - Timely technical publications

The client-confidential assignments conducted by The Catalyst Group include projects in:

- Reinventing R&D pipelines
- Technology alliances
- Technology acquisition
- Market strategy

We have built our consulting practice on long-term client relationships, dedication, and integrity. Our philosophy is clear and focused:

We Provide the "Catalysts" for Business Growth by Linking Technology and Leading-Edge Business Practices to Market Opportunities

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VI. DELIVERABLES AND PRICING

This report is timely and strategically important to those industry participants and observers both monitoring and investing in the development and implementation of membranes in separations for application in the refining, petrochemical/chemical and industrial gases industries. TCGR's report, based on technology evaluations, commercial/market assessments and interviews with key players goes beyond public domain information. As a result, subscribers are requested to complete and sign the "Order Form and Secrecy Agreement" on the following page.

The study, **"Membranes in Separations: Commercial Advances in Refinery, Petrochemical/ Chemical and Industrial Gases Applications"** was completed in November 2016 and is immediately available.

Membranes in Separations: Commercial Advances in Refinery, Petrochemical/Chemical and Industrial Gases Applications	**Price** $21,500
Report in PDF format, in addition to subscription price	$1,000

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Please enter our order for "**Membranes in Separations: Commercial Advances in Refinery, Petrochemical/Chemical and Industrial Gases Applications,"** completed in November 2016, as follows:

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FIGURES

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TABLES

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