Frontiers of Hydrocarbon Business – Molecules to Markets – One Perspective

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This paper gives a scientific perspective on the hydrocarbon business that provides energy and materials to the modern society enabling a higher standard of living. It illustrates how the application of fundamental science solves business problems and creates societal value.

Virtually all of the fuels, chemicals, and materials used by modern society are produced through chemical transformations. Chemical Reaction Engineering (CRE) plays a pivotal role in bringing molecules to markets in this value chain. Beginning from the fundamental science of molecular understanding, chemical transformations moving through process level engineering and culminating into plant and system level integration, CRE enables the value maximization of molecules through the technology chain (see Figure 1) to the point of enterprise value realization via commercialization.

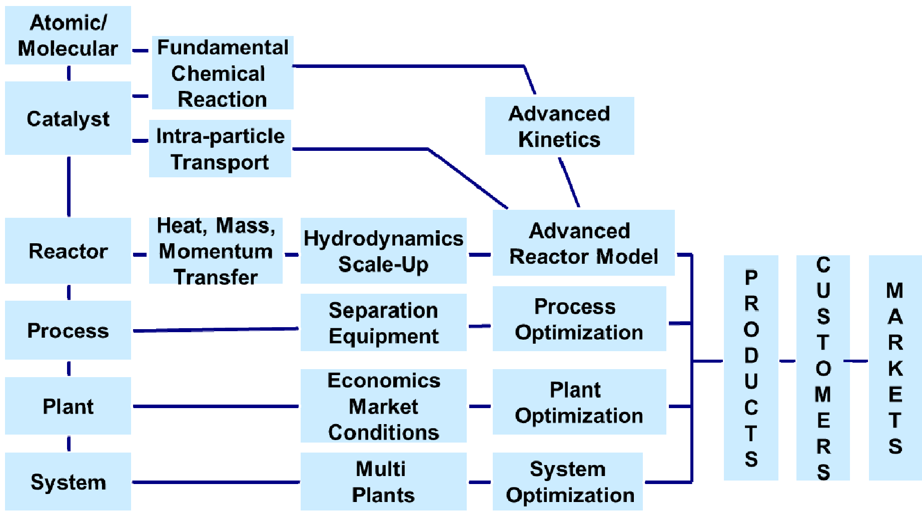


Figure 1: The technology chain to move molecules to markets through fundamental scientific/technological advances.

This paper reviews some of the work performed by the author in some critical technology areas in his career, which demonstrates how science can be converted to practical solutions that created commercial differentiation for some aspects of the hydrocarbon business.

Catalysis

Mobil was the first in the world to develop and introduce proprietary ZSM-5 as an additive in FCC units in the mid 80's to increase gasoline octane. The chemical transformations take place at molecular level in zeolite pores, which are at angstrom level. Mobil's intellectual property in zeolites for hydrocarbon transformations dominated this scientific field for decades. Today ZSM-5 additive is primarily added to increase propylene yield, a more valuable product, at the expense of gasoline. Increasing propylene production is important to develop variety of downstream products including polymers to meet growing demand from developing economies. Recently Reliance has developed a more active and stable ZSM-5 additive with a proprietary development. This development will increase 0.5% in propylene yield in each FCC, i.e., additional propylene of ~150 T/d, from the two FCC units, compared to the available commercial ZSM-5 additives from various suppliers.

Kinetics or Rates of Chemical Transformations

As an example of the importance of kinetics let us look at the methanol to olefins (MTO) process, developed in early eighties. This process produces primarily ethylene and propylene, the building blocks for the plastics industry. Novel experiments that varied space velocity to maintain constant reactor outlet conversion to compensate for catalyst aging were done to simultaneously study the kinetics and catalyst aging, for methanol to olefins (MTO) process in early eighties. Using the variable space velocity, aging and conversion kinetics can be decoupled (see figure 2). This accurate decoupling of conversion kinetics and catalyst aging enabled accurate prediction of cycle length for fixed and fluidized beds using the same kinetics parameters (Sapre, CES 1997).

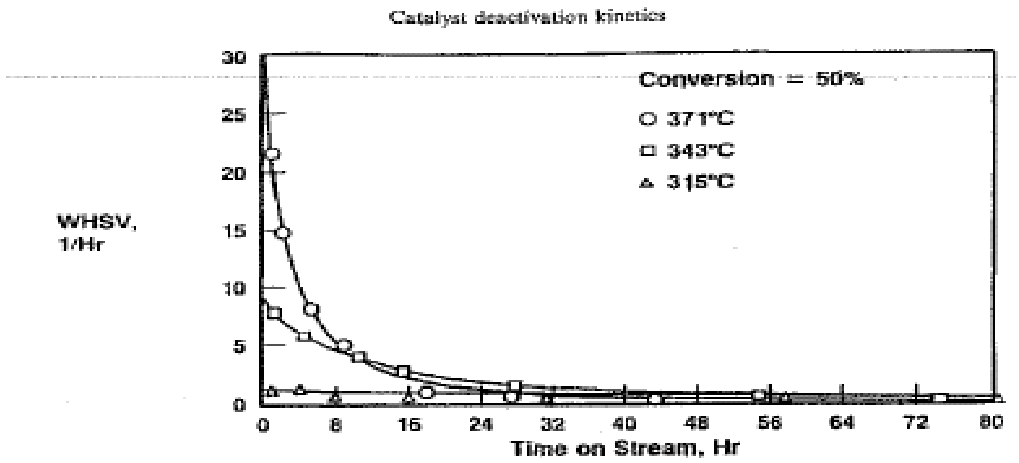


Figure 2: Weight hourly space data versus time on stream. (Sapre, CES 1997)

Methanol to olefins is an unusual reaction involving acceleration of methanol conversion due to autocatalytic effect of first formation of olefins. Interaction of autocatalysis and particle diffusion can lead to several unusual phenomena (see figure 3). We took advantage of this interaction to demonstrate that bigger particles lead to smaller reactor volumes. The autocatalysis also leads to reactor run away, multiplicity and oscillatory behaviour over certain operating parameters. Contrary to prevailing theory, these were unusual and unanticipated behaviour for a commercially important MTO reaction. In order to understand the fundamentals of autocatalysis/diffusion interaction we developed first principles theory that accurately predicted rate enhancement as well as reactor stability and helped optimize reactor design and scale-up.

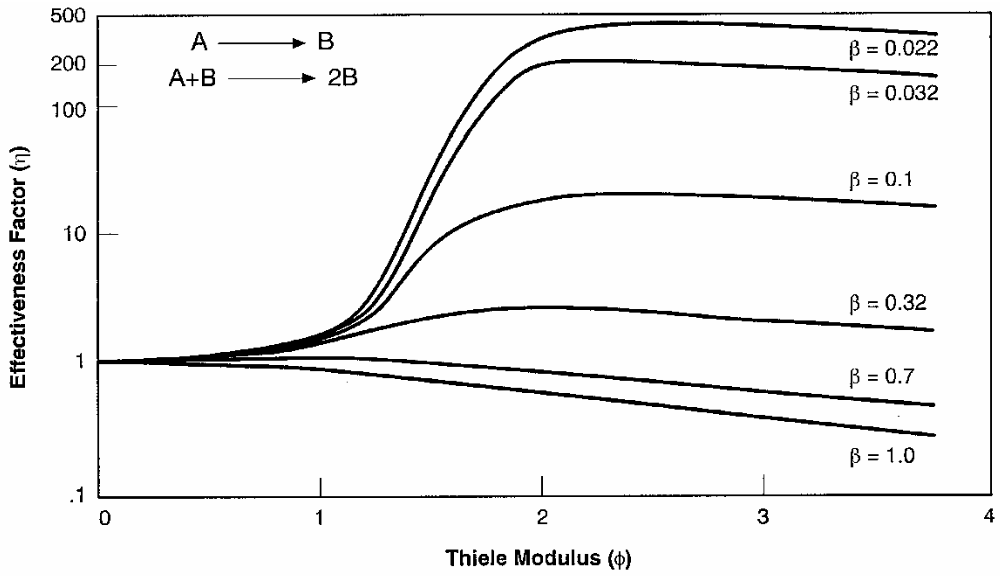


Figure 3: Particle effectiveness factor curves for quadratic autocatalysis. Here, effectiveness factor (η) is the ratio of integral average reaction rate of A in particle to reaction rate of A at surface conditions; and β defines the relative rate of the first reaction to the second reaction at zero surface concentration of B. (Sapre, AIChEJ, 1989)

Another major breakthrough was the detailed kinetics of complex mixtures such as crude oil. Molecular finger printing of crude oil (several hundred thousand molecules) is now possible with modern analytical technology. Feedstock is one of the largest contributors to operating cost and we need to maximize value of every molecule. Such rigorous representation of feedstock composition improves kinetics and product property predictions that improve accuracy of business decisions from planning to control.

As an illustration let's look at how kinetics of fluid catalytic cracking (FCC) process has evolved in the last fifty years. The kinetics representation of processes has evolved from simple 3 lump model to 10 lump model (see reaction network for FCC kinetics in Figure 4) to about 50+ lump models. In Mobil we developed a new approach called structure oriented lumping, which is essentially a molecular level representation of kinetics for complex mixtures involving thousands of molecules, typical of crude oil. With this methodology the kinetics can now be represented by group contribution methods, similar to thermodynamics. Such molecular group contribution models are significantly more accurate than lumped models creating enormous value, which is a major contribution to the field of kinetics.

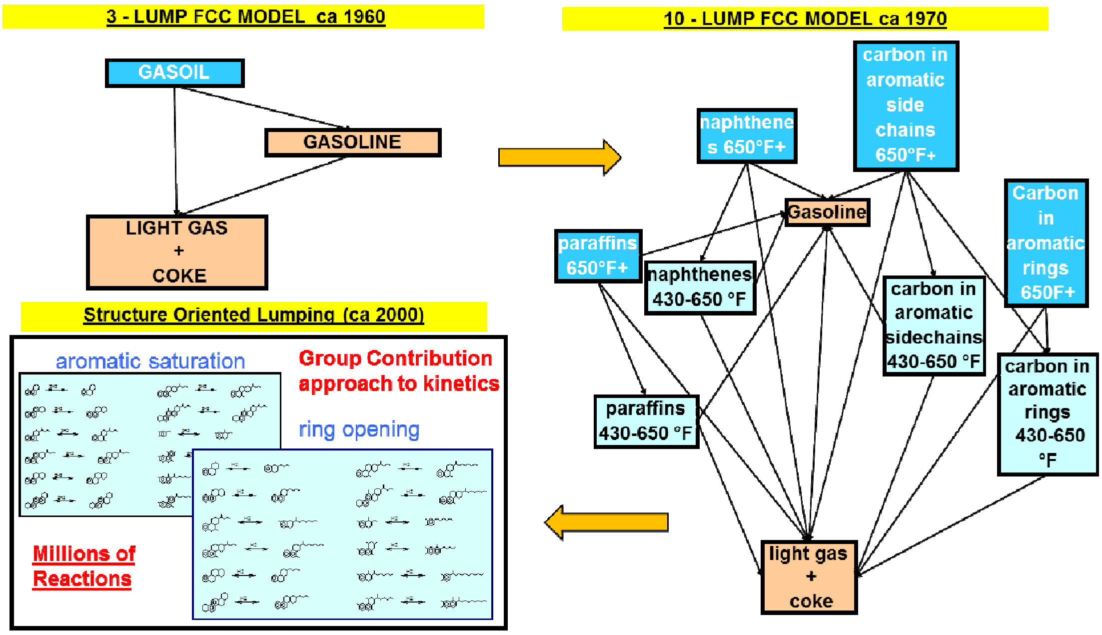


Figure 4: The evolution of FCC reaction kinetics modelling. Molecular composition models provide more accuracy than lumped models (Sapre, Kramback, 1991).

Group contribution type approach to kinetics is allowing accurate representation of chemical transformations, resulting in molecular representation of product streams, which allows accurate product property predictions. This approach eliminates traditional approach of correlative models, e.g., gasoline octane determination using engine test data. Now the composition models allow accurate prediction of such properties from individual molecular octanes. Impact on profitability of this approach when integrated with planning for crude selection and processing in refineries with advanced process control, real time optimization and rigorous planning scheduling tools is hundreds of millions of dollar per year for a large oil and petrochemical giant like ExxonMobil.

Reactor Design

We developed a rigorous theory comprising of constitutive equations to describe solids flow patterns in a dense fluid-bed FCC regenerators to help optimize regenerator performance. The key parameters of the constitutive equations were fitted with data obtained from probe measurements in operating commercial units. Integrated fluid mechanics models with coke burning kinetics allows to optimize the air grid design to match air flow with catalyst circulation patterns (see figure 5). This first principles approach helped improve the performance of commercial units by decreasing NOx by ~30% as it reduces after-burn. Also this design modifications increased the coke burning capacity by ~5%, and catalyst circulation, improving the overall FCC performance.

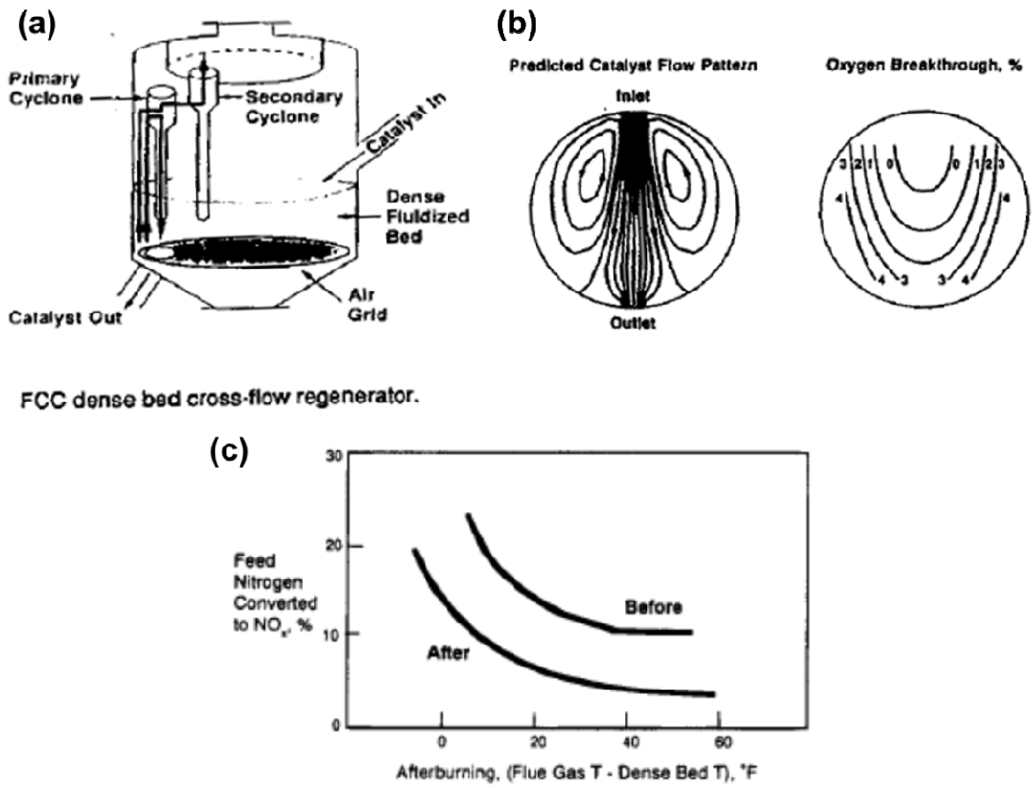


Figure 5: (a) FCC dense bed cross-flow regenerator, (b) oxygen breakthrough in cross-flow regenerators, and (c) improvement in performance as demonstrated by reduction in feed nitrogen conversion to NOx. (Sapre, Leib & Anderson, CES 1990)

Trickle bed reactor is the most widely used reactor system in the oil industry. We developed novel flow distribution measurement probes and installed them in large-scale commercial operating units. The results of our study showed significant point to point variation in liquid flow distribution. Our study also showed increase in non-uniformity of liquid flow moving down the reactor. Most significantly, contrary to popular belief, severe mal-distribution persists at high mass flow rate, e.g., so called pulsing flow regimes, and resulting poor process performance. Even today most commercial reactors are designed to operate in pulsing regimes with associated high capex and opex. We developed fundamental hydrodynamics models for multiphase flow by borrowing concepts like relative permeability, saturation and capillary pressure from upstream business (oil and gas reservoir models). The reservoir models flow patterns are typically at low Reynold's number, we extended this theory to turbulent flows typical of commercial trickle-bed reactors. We used the commercial and pilot plant data to fit the constitutive parameters. With this knowledge we developed, one of the most cost efficient reactor designs (lowest capex and opex design) and implemented them commercially.

The performance improvement of the newer trickle bed design is shown inFigure6. We fixed the efficiency from poorly performing design from 50% to almost perfect, close to 98%. In fact, commercial reactor process performance was better than the pilot plant.

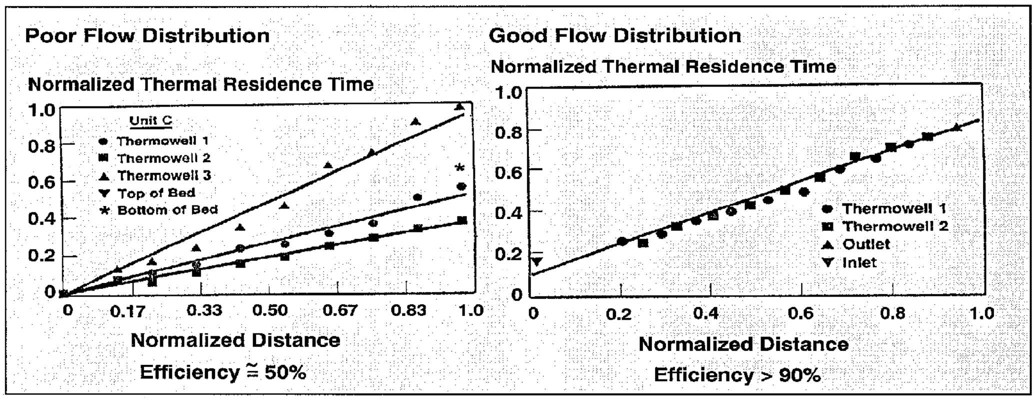
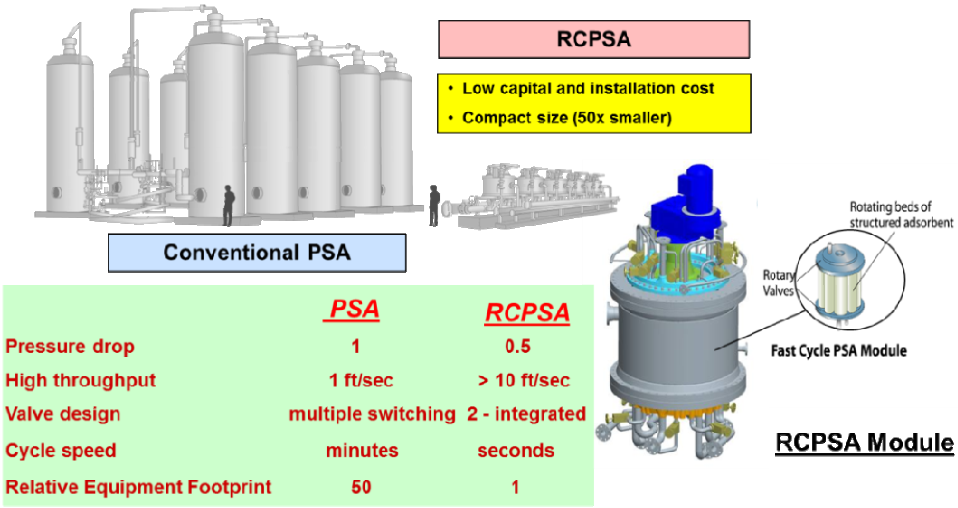


Figure 6: Fundamental understanding of phenomena on large scale system leads to significant performance improvement and efficient cost-effective reactor designs (Sapre & Katzer, I&EC Res., 1995)

Process Technology

TransPlus is a process and catalyst to trans-alkylate heavy aromatics, that otherwise go to fuel, to high value P-xylene, a key raw material for polyester production. In less than three years, we took this process from lab to commercial scale operation to maximize P-xylene. We were the first to develop and commercialize a trans-alkylation process in mid-nineties. Today several other licensors offer similar technology.

Another process innovation is a rapid cycle hydrogen purification process (RCPSA) that also involved development of a novel hardware. This technology development is an example of process intensification, where we reduced the size of the plant by almost a factor of 50. Rapid Cycle Pressure Swing Adsorption (RCPSA) offers a more compact, less expensive, and more energy efficient solution for H_2 recovery compared to conventional Pressure Swing Adsorption (PSA) technology (see figure 7), used commonly in the industry. We implemented this process commercially in France in 2007 and it won the coveted R&D 100 award in the USA in 2007.



	PSA	RCPSA
Pressure drop	1	0.5
High throughput	1 ft/sec	> 10 ft/sec
Valve design	multiple switching	2 - integrated
Cycle speed	minutes	seconds
Relative Equipment Footprint	50	1

Figure 7: Rapid Cycle PSA (RCPSA) commercial unit. Winner of R&D 100 award, in 2007

Plant Integration

Although advanced control and real time optimization tools have improved manufacturing performance over the years, these systems are an integration of several legacy systems. There is a significant opportunity to conceptualize step-change in optimization/control, both off-line and on-line using more rigorous tools. Optimization and control needs to be event driven to fully exploit manufacturing assets, and to fully sweat the assets. Here is an example of how we improved the performance for a utilities system (steam and power production).

The generation of steam and power required for the operation of a modern refinery is a significant operating cost – almost 10% of crude processed. We automated the entire power plant operation by developing a rigorous non-linear model for every piece of equipment and essentially automated with minimum operator involvement. Both non-linear programming and mixed-integer non-linear programming tools were employed and they replaced the legacy linear programming optimization technique. The results of this change are shown in figure 8, where top line is plant performance before the system and the bottom line is after the system was installed. We realized approximately 3-4% savings in fuel consumption amounting to a significant cost reduction. This system was named OPTIMUS – optimization of utility systems.

We also did a lot of work for the upstream oil and gas business. We were the first to integrate reservoir models with surface processing facilities and made significant progress towards developing fully integrated enterprise wide modelling tool. A software tool that integrated surface facilities with reservoir simulation was called OPTINET and used extensively to optimize tertiary oil recovery in Bakersfield, California. This increased tertiary oil recovery by 2-3%, reduced steam flooding, and extended the life of the oil field.

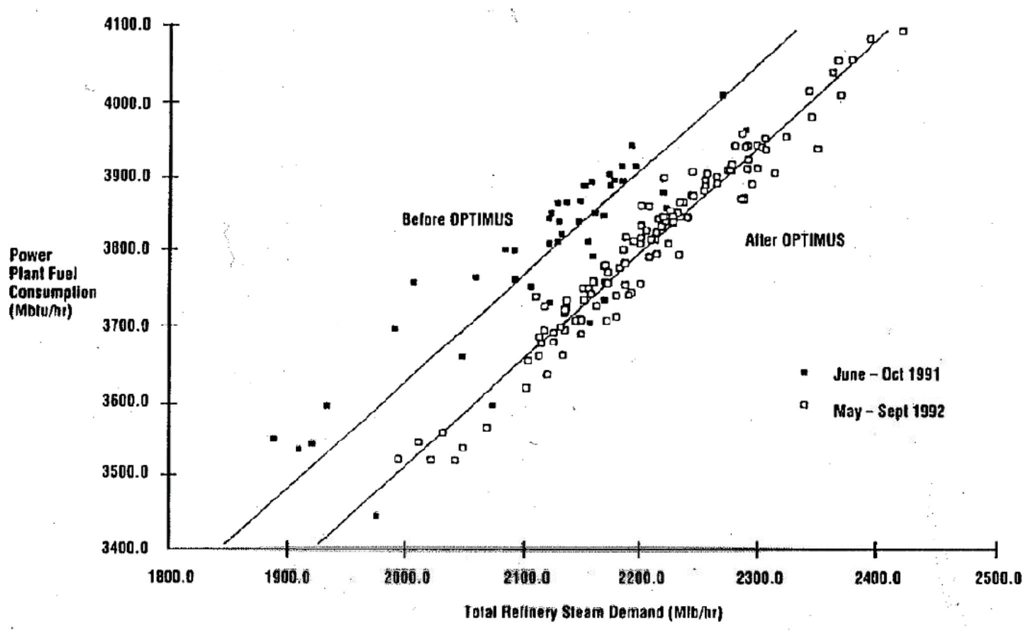


Figure 8: OPTIMUS: Improved performance at Beaumont Refinery with reduced fuel consumption (Wellons, Sapre, NPRA, 1984)

Figure 9 shows an enterprise wide optimization scheme increasingly possible with the help of technical computing with an expansive knowledge management framework.

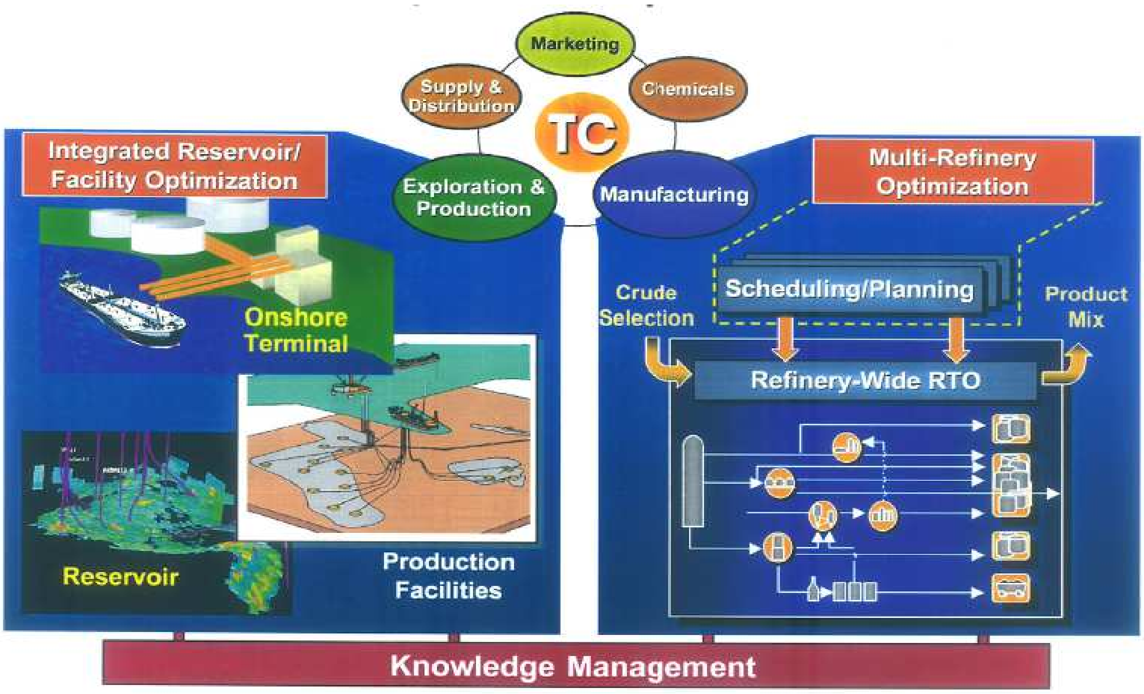


Figure 9: Application of knowledge to improve business in real time. (Katzer, Ramage, Sapre, CEP 2000)

Today, we have embarked upon end to end manufacturing digitization through world-class scalable IT backbone. Four key elements of this strategy are (i) process automation; (ii) cloud computing; (iii) mobility and usability; and (iv)big data analytics. The objective is to create a real time, online, integrated, connected, agile self-aware asset management system. In the near future, every industrial company will be a software company to create most value through access to massive real time data, and taking smarter business decisions.

Systems Analysis

One of the most challenging problems of our time is to develop alternative feedstock for the energy and hydrocarbon industry. The fossil fuel rich path taken by the developed world for its growth is not sustainable in the long run given the environmental constraints that the world faces now. The rest of the world, especially India, has the opportunity to leapfrog the developed world by adopting more sustainable energy technologies such as wind, solar or biomass (see figure 10). Integrating new streams of energy and feedstock with the existing infrastructure is an ideal system level problem.

One promising biomass energy resource is algae that convert CO_2 and sunlight into oil. Algae have the highest productivity. With rapidly advancing biotechnology, it is likely to lead to a commercial viable option in the near future, which may make India self-sufficient in liquid hydrocarbons. It is a reaction engineering problem, essentially multiplying reactors or algae cells, in a cultivation system or a large pond. The challenge is the efficient scale-up of biological systems to large scale industrial applications. However, we are making steady progress in unravelling the mystery of photosynthesis and increase overall sunlight to biomass energy productivity significantly.

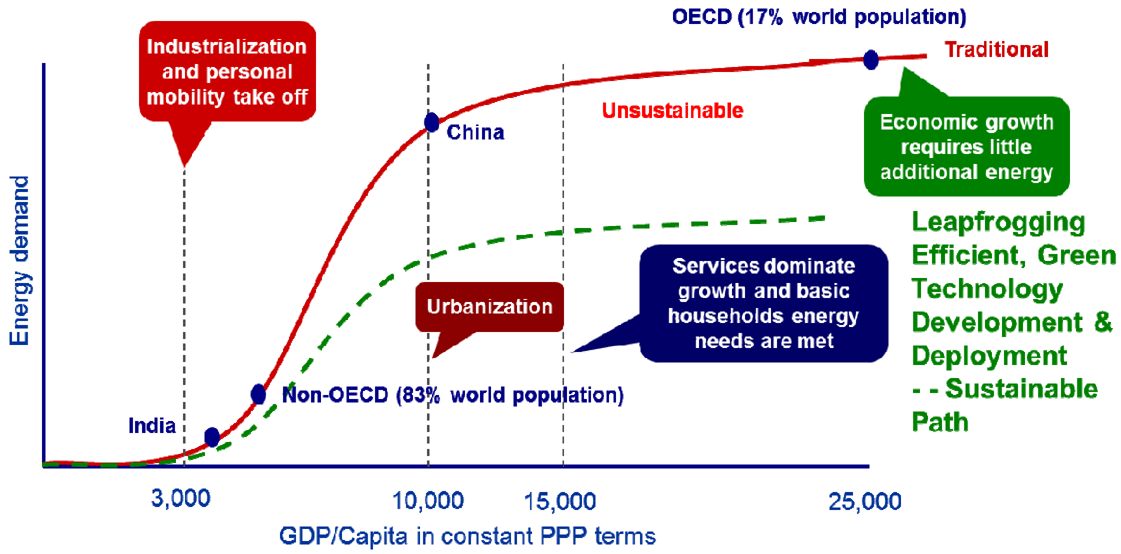


Figure 10: Demand for energy is growing rapidly as countries like India enter the most energy-intensive phase of economic development.

Conclusions

The boundaries between what we know, understand, and can quantify and what we cannot yet adequately quantify defines the frontiers. As the technology chain matures and we solve the problems, there are advances in frontier areas at all levels. It leads to closer integration of fundamentals from the molecular level through to the system level optimization creating societal value through life enriching projects.

The global drivers of environmental sustainability and providing growth opportunity to the 80% of the world population living in the developing countries demand a paradigm shift in the direction we require to shift the frontiers of science and technology. In the context of India, where we have a challenge of improving quality of life across entire socio-economic spectrum, in agreement with the motto of the current government – Sabke Saath, Sabka Vikas, "inclusive innovation" that will create affordable excellence is the call of the day for scientists and engineers.

It will require a concerted effort across the boundaries to cater to the diverse needs of the nation- food, infrastructure, healthcare, material and energy needs of the masses, automotive, defence and space. We should aim to achieve "affordable excellence". Industry excels at execution and research institutions excel at creativity. We must intertwine our resources to help India leapfrog into the future, with a collective mandate: Science for Solution; Technology for Transformation; and Innovation for Impact.

"I would prize every innovation of science made for the benefit of all" – Mahatma Gandhi

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