Optimize Refining Operations Using Plant Digital Twin Based on Molecular Modeling

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Introduction

Energy depletion is one of humanity's top problems. Finding ways to use petroleum resources while meeting the increasing demand for high-quality products — and environmental regulations — is one of the keys to the energy crisis. Energy companies need to maximize overall profit at the enterprise level while meeting the current customers' requirements to resolve this crisis. Optimization in refineries is no longer limited to a single unit or process, a single piece of equipment or even a single refinery, but often considers a comprehensive scope including multiple refineries, units, processes, equipment and so on as shown in Figure 1. We call this scope "smart refining."
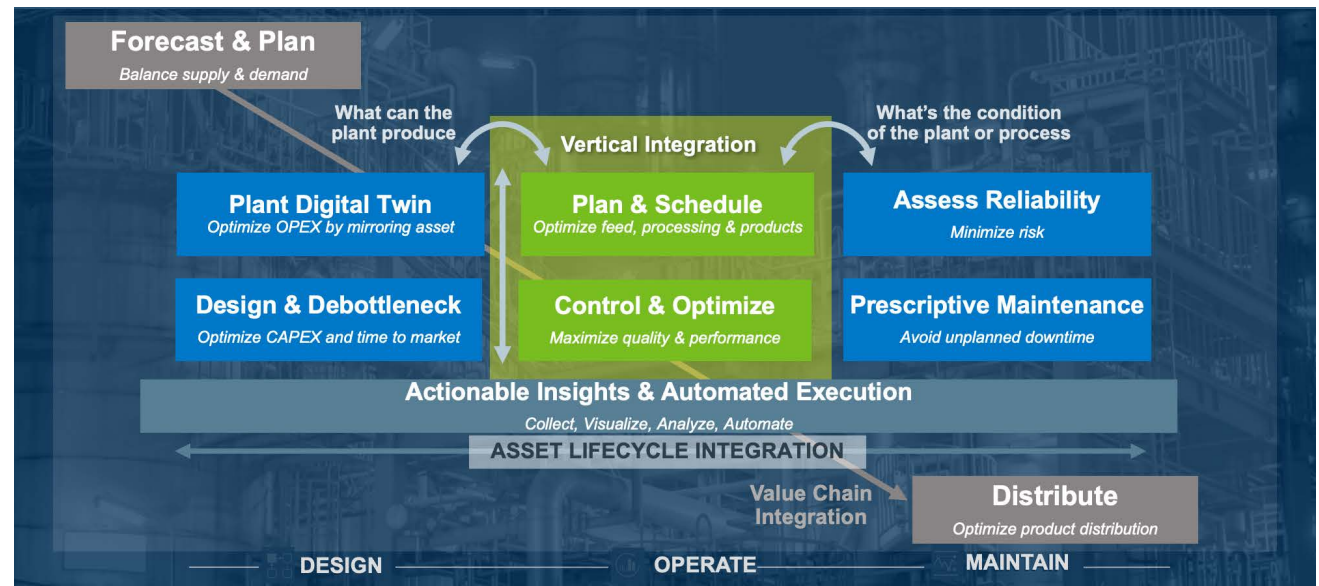

Figure 1. A vision of smart refining

Unlike traditional process optimization, smart refining considers multiple processes together and extends the system to other dimensions: analytics, risk prevention and the optimization of equipment. In smart refining, every single chemical process is digitally modeled and integrated with other processes and relevant equipment to achieve complete asset optimization. Smart refining centers around optimizing across multiple process units at multiple scales and various scopes to obtain a unified optimization, as shown in Figure 2.

Figure 2. A unified process and asset optimization for smart refining

The system will consider a set of optimization problems for multiple time scales. For example, at a monthly or weekly level, we need to optimize planning and scheduling of one or more refineries to find the best scenario for achieving maximum profit while minimizing the cost of purchases, operations and maintenance. Once we've identified that scenario, the plan is sent to plants to operate and optimize at a daily or hourly level (e.g. real-time optimization). For each individual plant, we can further optimize, using advanced process control (APC) to maintain or run the plant stably and smoothly and reach the best operating point.

In addition to the various time scales, the system will need to model a variety of plants in one refinery or across multiple refineries together. The best example is an optimization of the integration of refining and petrochemical processes.

The refining industry's trend for the next decade is to shift from being fuel-oriented to being raw material-oriented. The most important question in the field of energy and fuels is how to effectively and efficiently utilize petroleum oil, the major resource in the earth. New alternative oil, such as shale gas/oil, mean the demand for fuel no longer depends as greatly on petroleum oil. However, the increasing demand to use every carbon atom in petroleum hydrocarbon mixtures as raw feed for petrochemical processes is becoming more significant. Therefore, tools integrating refining and petrochemical processes will be the next generation technology for refiners.

For example, ExxonMobil had already succeeded in this area, inventing and industrializing a technique for direct steam cracking of crude oil.[1] More refiners in the world are planning to develop new technology or change the operation of their plants based on the crude-to-chemicals trend: Saudi Aramco, PetroChina, ZPC and so on. However, the traditional lumped model strategy cannot solve the upcoming dilemma in the crude-to-chemicals processes.

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1   "Why the Future of Oil is in Chemicals, Not Fuels." Alexander H. Tullo, *Chemical & Engineering News* Vol. 97, issue 8, Feb. 25, 2019.
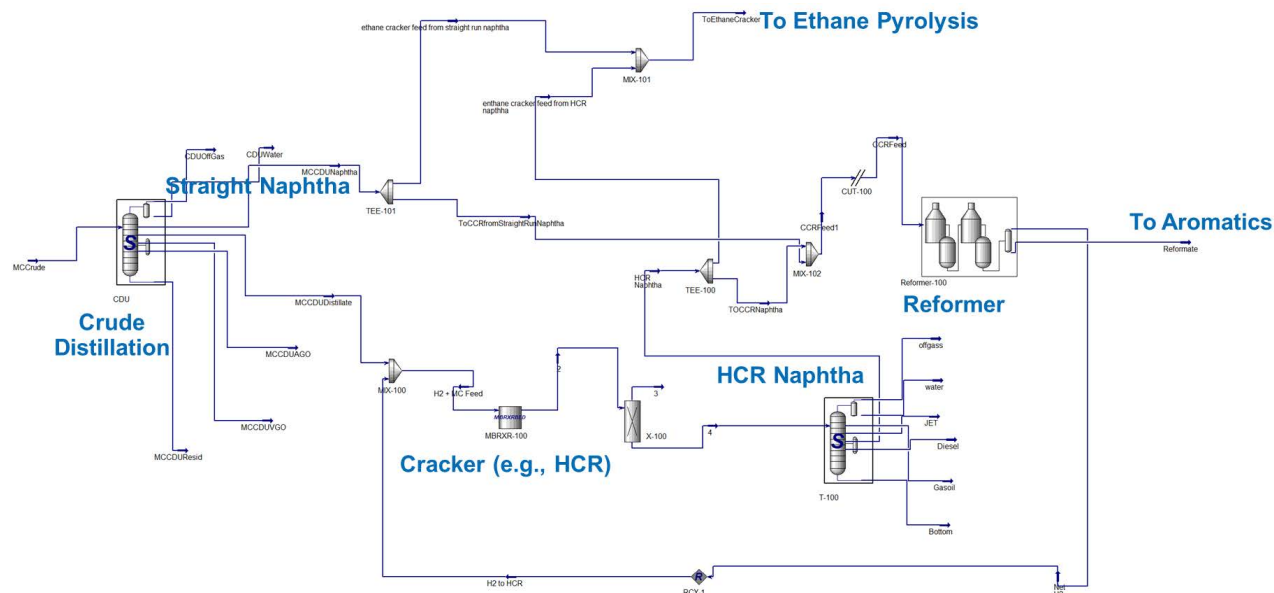
Figure 3. Representative refinery simulation model for refining and petrochemical integration

Figure 3 shows a typical flowsheet of the integration of refining and chemicals. Crude oil first goes through a crude distillation unit (CDU) to separate into various boiling fractions: straight-run naphtha, distillate, atmosphere gas oil (AGO), vacuum gas oil (VGO) and residual oil. The middle or heavier fraction (e.g. distillate) is upgraded through reactors (e.g. a hydrocracker) to produce the upgraded fractions (e.g. HCR naphtha). Moreover, light fractions from different plants (e.g. naphtha) can be further upgraded through reactors (e.g. reformer) and transformed into desired products.

Unlike the traditional refinery, crude-to-chemicals products are not solely fuels, but the naphtha fractions are the feedstocks of petrochemical plants (e.g. ethane cracker and aromatics production). The typical scope of optimization is a single unit, such as a CDU, reformer, or hydrocracker or a few units. For a crude-to-chemical scope, however, the operator needs to move beyond the unit level to consider optimization across both the refinery and the chemical plant.

However, the traditional lumped model approach cannot solve the optimization of the flowsheet shown in Figure 3. The lumped models used in refining usually define their species by physical properties (such as boiling point or solubility) as shown on the left of Figure 4. The model lacks data on the essential chemical structure. As a result, the lumped model cannot represent the species beyond its definition. However, the species used to model a petrochemical plant are molecular components, shown on the right of Figure 4.

In order to model refining units and petrochemical units together, we need to describe precisely the molecular species on the right of Figure 4 from the refining units. The lumped model is unable to provide this function and thus blocks integrating the optimization of crude-to-chemicals processes. In addition, the lumped model typically requires some simplifying assumptions of the chemistry. As a result, we cannot gain a deep understanding of the refining chemistry and catalyst parameters, and we are unable to obtain an optimal conversion for a reactor.

Figure 4. Challenges to model refining and petrochemical integration
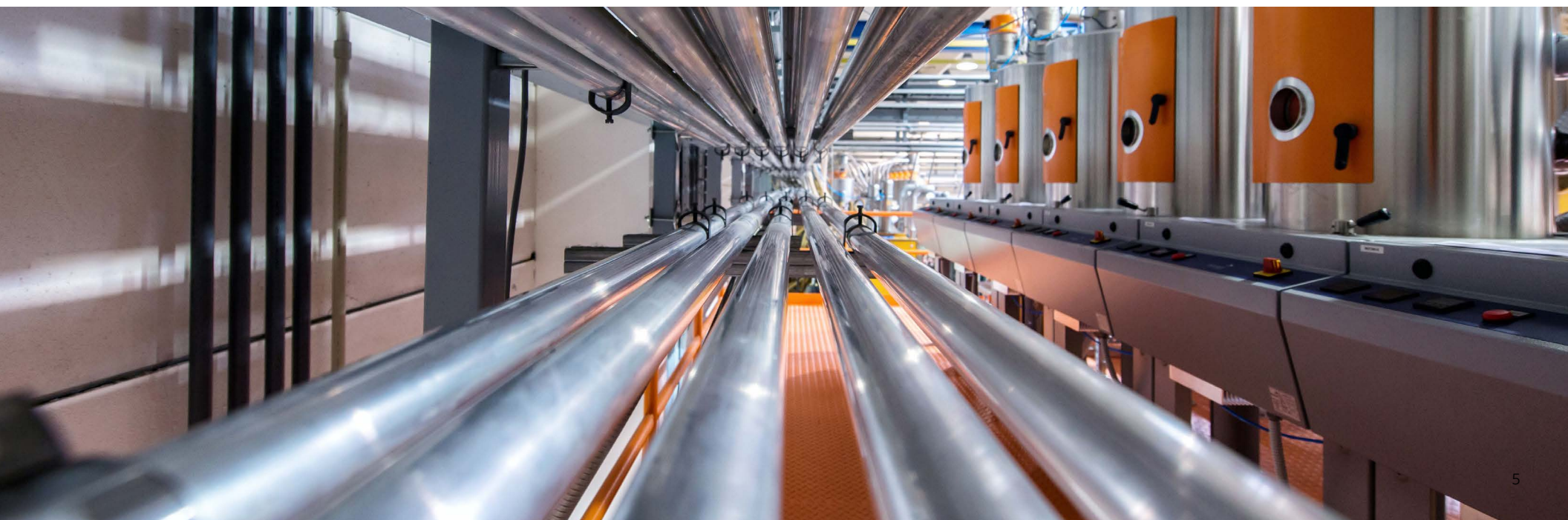
For example, deep hydrodesulfurization (HDS) requires us to clearly describe the different structures of sulfur molecules and their reaction pathways. Similarly, isomerization or FCC-MIP (maximum isoparaffin in fluidized catalytic cracking) requires us to represent isoparaffin structures and their reaction networks. What's more, due to the increasing demand for high-quality products, the property model needs to provide much more accurate estimations to support process models.

The lumped model limits us to using state-of-the-art property models when the task at hand explicitly requires chemical structures. The integration of refining and petrochemicals requires not only knowledge of how the refining stream can propagate to petrochemicals; it also requires a good representation of the chemistry at the molecular level for every refining reactor unit. We have developed a new approach to address this issue: molecular level modeling.

Creating Molecular Models of Complex Refining Chemistries

As the fundamental feature in refining, molecules can reveal the nature of chemical conversions in refining chemistries. In addition, we can apply a property model at the molecular level to obtain high-quality predictions of selected important properties. As a result, molecular-level modeling can provide an optimal solution to utilize the resources in a wide range of refining and chemical processes to deliver both the yields and qualities of products refineries need to maximize profit.

In past years, several groups have dedicated research in this field, including teams from ExxonMobil, Froment and co-workers, Klein Research Group (KRG), the French Institue of Petroleum (IFP Energies Nouvelles or IFPEN), University of Manchester Institute of Science and Technology (UMIST) and China University of Petroleum, Beijing (CUPB). The appendix briefly introduces these groups. Most of these groups, aside from ExxonMobil, are in universities or research institutes. As their research activities are academically focused, it is not always straightforward to apply their research directly to practical industrial applications. ExxonMobil, however, has obtained significant business benefits through their internal molecular modeling technology.[2]

Refiners need a third-party supplier to provide an integrated industrial solution that allows them to apply molecular modeling to smart manufacturing and obtain business success. As the leader in the field of process simulation and optimization, AspenTech started to develop a molecular modeling framework in 2011, focused on providing a software framework and industrial solution to refiners. The framework contains two key technologies: molecular characterization (under assay management) and molecule-based reactor models (under refinery modeling). The following sections describe the two technologies in details.

[2]   ExxonMobil Annual Report, 2012.

Molecular Characterization (MC)

AspenTech starts with feedstock characterization at the molecular level, or molecular characterization (MC)[3,4,5]. MC is a novel, practical and comprehensive molecule-based approach to characterize crude oil and petroleum fractions for correlation, prediction and estimation of assays and properties of crude oil, crude oil blends, petroleum fractions, condensates and petroleum mixtures. This approach provides a systematic methodology that determines the numbers and types of modeling molecules and their compositions to broadly represent chemical and physical properties of crude oil and petroleum fractions.

Molecular characterization uses a set of model compounds to represent the species in a sample containing crude oil or petroleum fraction (feedstock). AspenTech has constructed a library of model compounds that covers the wide range of compound classes, structures and boiling ranges known or postulated to exist in crude oils. The properties for each model compound are estimated using known or AspenTech proprietary methods. When analyzing a feedstock with traditional assay data and detailed molecular-level data, MC will select a set of model compounds from the library and determine compositions of these model compounds to represent this feedstock, thus creating a molecular-level "model" of the feedstock. A complete description of the molecular characterization method can be found in the patent application.[5]

3   "Method of Characterizing Chemical Composition of Crude Oil for Petroleum Processing." Chau-Chyun Chen and HuiLing Que. United States Patent US20130185044A1, 2013.
4   "Method to Represent Metal Content In Crude Oils, Reactor Feedstocks, and Reactor Products." Suphat Watanasiri, Shu Wang and Lili Yu. United States Patent US20160162664A1, 2016.
5   "Molecular Characterization Method and System." Suphat Watanasiri, Shu Wang, Lili Yu and Christopher Quan. United States Patent Application, Docket No. 1086.2060-000

Explore the key innovations of the molecular characterization technology further:

- Data measurement protocol

- Library of model compounds

- Properties estimation for model compounds and mixtures

- Selection of model compounds to represent feedstock

- Algorithm to process assay data

Data measurement protocol

The figure below shows a protocol for measuring petroleum fraction and crude oil samples to provide the data necessary for MC to develop a molecular-level model of the samples. Such a protocol can serve as a good starting point for any company that is interested in creating a program to manage oil sample measurements at the molecular level. Since the field of petroleomics (characterization of petroleum and crude oil using high resolution mass spectrometry) is quickly changing, the protocol is expected to change and improve as well.

This protocol involves many measurement techniques. The traditional assay measurements include distillation (TBP) curve, bulk properties such as density curve, sulfur content curve, PNA distribution, octane number, cetane number, viscosity, etc. The molecular-level measurements include gas chromatography/mass spectrometry (GC-MS) for light cut range (<200C), gas chromatography/time-of-flight mass spectrometry (GC-ToF) for medium cut range (200-350C) and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) for heavy cut range (>350C).
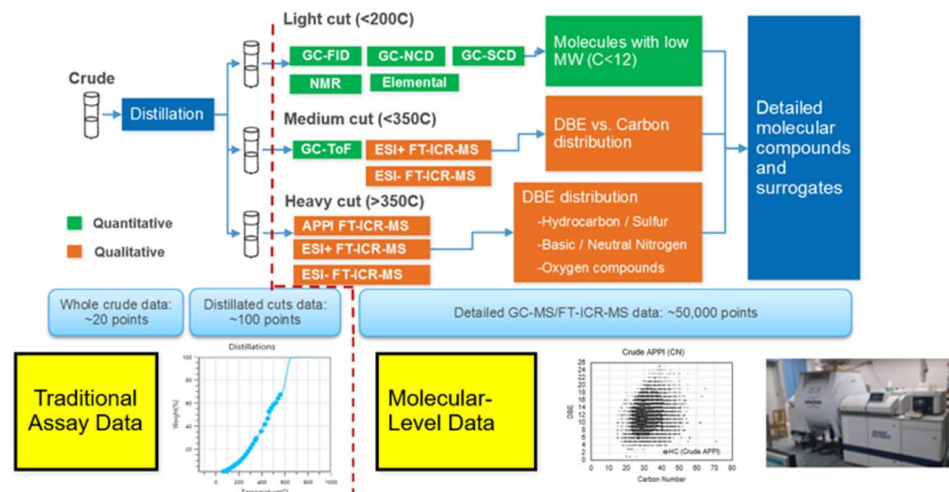
Figure 5. Data measurement protocol at the molecular level

The GC-MS measurement identifies light-end components and compounds in the Naphtha range, which can be used directly to determine compositions. The GC-ToF measurements provide quantitative information: compound types in terms of double bond equivalent (DBE) and carbon numbers and intensity which are used to determine distribution function parameters for hydrocarbons. The FT-ICR MS measurements provide qualitative information: relative intensity in terms of DBE and carbon numbers for hydrocarbons and other hetero-atom types.

Future advances in instrumentation may provide quantitative data, which will be more useful and can be easily adopted in the protocol. The MC framework can process these different types of measurements and consolidate them using a patent-pending algorithm to create a molecular level model of the crude or petroleum fraction sample.[5]

Library of Model Compounds
A prerequisite to this process is a model molecule database covering a wide variety of classes. The library includes compounds selected based on their thermodynamic stability and with structures known or likely to exist in crude oils, feedstocks and reactor products:

Paraffins	Naphthenes
Aromatics	Olefins
Mercaptans	Thiophenes/Sulfides S1
Thiophenes/Sulfides S2	Sulfoxide/S1OX
Sulfur-Oxygen/S1OX	Neutral nitrogen N1
Neutral nitrogen N2	Neutral nitrogen sulfur N1S1
Neutral nitrogen oxygen N1Ox	Basic nitrogen N1
Basic nitrogen N2	Basic nitrogen sulfur N1S1
Basic nitrogen oxygen N1Ox	Phenol
Paraffinic acid	Aromatic & Naphthenic acid
Vanadium porphyrins	Nickel porphyrins

Table 1. Model compounds in MC

Properties Estimation for Model Compounds and Mixtures
Compound properties of interest include normal boiling temperature, density, and elemental properties such as sulfur content, nitrogen content, etc.

The normal boiling temperature and liquid densities of the compounds are calculated using the PC-SAFT equation of state the elemental properties such as sulfur content, nitrogen content, carbon content and hydrogen content are calculated directly from the molecular formula.[6] Other physical properties are estimated using various formulae and correlations.

Selection of Model Compounds to Represent Feedstock
A process has been developed to systematically select a set of model compounds from the library to represent the feedstock of interest. Not all compounds available in the library are required to describe the properties for a given assay. The compound selection process depends on the types and qualities of data available.

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6   "Modeling Polymer Systems Using the Perturbed-Chain Statistical Associating Fluid Theory Equation of State." Joachim Gross and Gabriele Sadowski. *Industrial &Engineering Chemistry Research*., 41, 1084-1093. September 21, 2001.

The primary method for compound selection uses distributions of conceptual segments, which represent the molecular classes to determine the probability of the compounds in a given class existing in the assay sample. The conceptual segments were chosen to represent all molecule classes and structures considered.

An important concept of molecular characterization is called "molecular profile." A specific molecular profile is associated with a sample assay for either a crude oil or a petroleum fraction. The profile consists of the following key information: relative weight of each compound class, conceptual segment types of each class, the segment distribution information for each segment and viscosity parameters. This collection of information is unique for each sample assay and is used in molecular characterization to represent the model compounds selected from the MC library and the compositions of these molecules. The molecular profile, in essence, represents the molecular-level "model" of the crude oil or petroleum fraction.

Algorithm to Process Assay Data

The program will use all the data to select compounds from the MC library and compute compositions based on the segment distribution functions and their parameters set from experimental data during the characterization process.

Once a unique set of compounds with their compositions is obtained, the program will calculate bulk assay properties using properties for each compound and mixing rules corresponding to the property. Comparing the calculated bulk properties with measured bulk properties, the errors between these two are used to construct the objective function. Then the program uses an optimizer to adjust certain parameters to minimize the objective function in an iterative process until convergence is achieved.

At convergence, the final set of compounds with their compositions are obtained such that the calculated bulk properties are close to the measured bulk properties. This set of compounds with compositions also matches closely the molecular-level measurements of the sample using GC-MS, GC-ToF, Nitric Oxide Ionization Spectrometry Evaluation (NOISE), and/or FT-ICR MS methods. Figure 6 illustrates this iterative process.
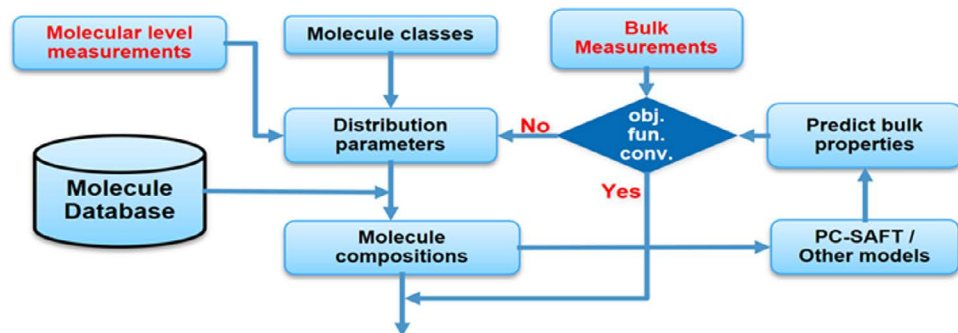
Figure 6. The AspenTech Molecular Characterization workflow

The molecular "model" of the sample assay can then be used to predict other properties using the underlying compounds and their properties. Figure 7 shows some of the properties the model calculates. The assay model can be stored in an assay library and may be used in a flowsheet simulation including reactors.
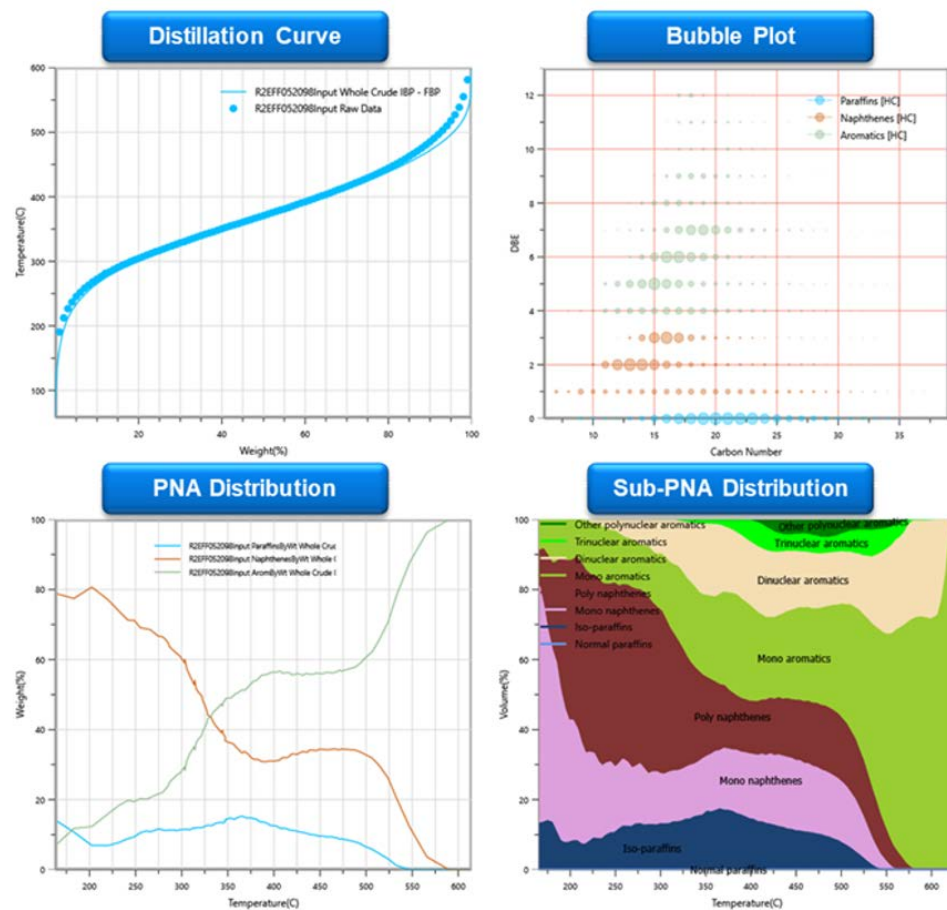
Figure 7. Representative results from Molecular Characterization

Molecule-Based (MB) Reactor

Since the MC technique provides a clearer identification of molecular details quantitatively or semi-quantitatively for the petroleum fractions up to heavy oil based on state-of-the-art analytical techniques, it provides a solid scientific basis for developing a molecule-based reactor model in refining processes. In this paper, we use a typical molecule-based (MB) hydrocracker (HCR)/hydrotreater (HTR) to illustrate the technical highlights of the molecular reactor model.[7] Table 2 shows a summary of the benefits of an MB HCR/HTR.

Customer Interests	Required specs	Conventional Reactor	MB Reactor
High accuracy model of selected properties Integration to petrochemical	Identify branched isomers of PIONA	Only supports empirical correlation	Includes detailed branched molecular species
Deep understanding and optimization of refining chemistries	Describe more realistic kinetic and mechanism	Not supported	Detailed reaction path: isomerization, HDS
Catalyst design and development	Intrinsic kinetic parameters	Not supported	Obtains more intrinsic kinetic parameters of catalyst Less dependent on flowsheet, feedstocks
Resid processing	Describe heavy end conversion	Not well-supported	Includes archipelago resid structure and reactions
Apply user's in-house kinetics and reactor models	Allow users to add or edit components, reactions, kinetics	Not supported	Automates code generation for user's in-house components, reactions and kinetics
Propagation of detailed high quality data of reactors to PIMS	Estimate molecule-based structural properties	Not supported	Supports estimations of molecule-based structural properties
An optimal way to provide high quality data to machine learning model	Process data (measurable and not measurable) of all necessary dimensions	Not well-supported	Inherently provides densified data and reveals most important data among complex chemistries

Table 2. New benefits and specificationss of an MB HCR reactor

7   "Molecule-Based Equation Oriented Reactor Simulation Infrastructure And Its Model Reduction." Zhen Hou and Darrin Campbell. United States Patent Application, Docket No.: 1086.2062-000. 2019.

Nowadays, in addition to seeking accurate predictions of a refining conversion unit's product yields, refiners are showing greater interest in the qualities of the products themselves. Many important properties (e.g. research octane number, motor octane number, cetane number, etc.) are strongly related to the molecular structures in a product stream. While a traditional lumped model cannot use state-of-the-art property methods to predict those properties, it is very straightforward for molecule-based modeling to do so.
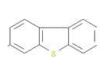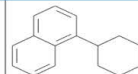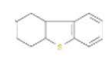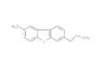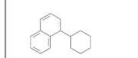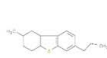
In addition, with more detailed isomeric information, the molecule-based model can assist with integrating and optimizing refining processes and petrochemical processes. Because the molecule is the fundamental feature in hydrocarbon conversions, an MB model can reveal the detailed mechanism of a conversion and provide a deeper understanding of refining chemistries.

For example, an MB reactor has the capability to describe the detailed paths of deep hydrodesulphurization (HDS) and isomerization. With an MB reactor, refiners can utilize more intrinsic kinetic parameters of the catalyst for a refining conversion unit. As a result, the model can depend less on the variations of flowsheets and feedstocks. Alternatively, an MB model provides a much wider prediction range to users. The traditional lumped model has a limited capability to process heavy feedstocks due to its inability to describe the feed beyond its lump definition. An MB model provides good support for describing resid processing.

To reduce the complexity of applying an MB reactor, we developed a model-building tool to deliver different reactor models without hard-coding chemistry for a specific unit. Planning and scheduling tools (e.g. Aspen PIMS™) use a base delta LP submodel for optimization. An MB model can provide high quality data to Aspen PIMS at the molecular level, so the user can create more accurate submodels. In summary, the high resolution rigorous predictive model of an MB reactor provides high-quality solutions for refining processes. In the next sections, we will briefly introduce the technical details of the MB reactor.

A set of homologous series was used for the MB reactor to describe the molecular components in refining hydrocarbon mixtures. Figure 8 shows an example of molecular components for a hydrocracker (HCR).

Figure 8. A homologous series of hydrocracker molecular compositions

In Figure 8, each column represents one series containing a unique molecular type. The molecular types have significant reactivity and thermodynamic properties and thus determine the product quality and yields of the hydrocarbon conversions. Each row of Figure 8 is the continuous carbon number extension for the corresponding molecular type. The juxtapositions of the molecular types and carbon numbers represent the molecular composition of a hydrocarbon mixture.

The molecular species in MB modeling includes two parts. As shown on the left side of Figure 8, it is the representation of molecular components in a feedstock which is provided by AspenTech MC directly. Starting from the feedstock's molecular composition, we can derive the molecular composition of the HCR products via HCR reactions and kinetics.

Applying typical hydrocracking reactions shown in Figure 9, we obtain the updated product species for this HCR example. The product composition then updates back to MC. Therefore, this description is self-consistent with AspenTech MC. Finally we obtained 2623 molecular species including 2431 molecular components for HCR/HTR and 192 individual naphtha molecules by using the Kinetic Model Toolkit (KMT), a toolbox to generate detailed reactions and species, from the University of Delaware's Klein Research Group.
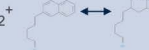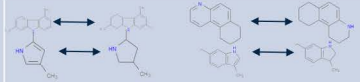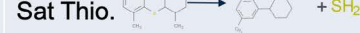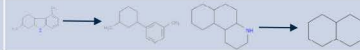
Reaction Family	Example	Comments
PAH Saturation	Sat6H $\quad 3H_2^+$ Sat4H $\quad 2H_2^+$	Saturate aromatic ring to naphthenic ring
Thiophenic Saturation	Sat6H $\quad 3H_2^+$ Sat4H $\quad 2H_2^+$ Sat2H $\quad H_2^+$	Saturate aromatic ring fused with thiophenic ring to naphthenic ring
Pyridinic or Pyrrolic Saturation		Saturate aromatic ring fused with pyridinic /pyrrolic ring to naphthenic ring
HDS	HS Thio. Sat Thio. $\quad + SH_2$ $+ SH_2$ $+ SH_2$	Remove sulfur
HDN		Remove nitrogen
RingOpen	H_2^+	Break up a naphthenic ring
Deaklylation/SidechainCracking	H_2^+	Break up the side chain attached to rings
Paraffin isomerization		Isomerize paraffins
Paraffin hydrocracking	H_2^+	Crack long chain paraffins to short chain paraffins
ILCR	H_2^+	Break up the inter-core linkages

Figure 9. Major hydrocracker reaction families

In order to validate the molecular species we set up for the MB HCR model, we compared our molecular compositions with the detailed analytical MS data. In this case, we used NOISE data. We selected the NOISE data of two oil samples (AGO and LVGO) acquired by AspenTech. The NOISE data provides the mass fractions of every data point in term of a molecular formula.

We mapped every MS data point to our molecular compositions without any adjustments and then simulated the distillation curve based on the properties of MB molecular compositions shown as the blue curve in Figure 10. The red curve in Figure 10 shows the experimental distillation curves. In Figure 10, the distillation curve derived from our molecular species has good agreement with the experimental data, so it demonstrated that our 2623 species can effectively describe the molecular information of a petroleum oil fraction. Then we applied the reaction families shown in Figure 9 to generate a comprehensive reaction network for hydrocracker/hydrotreater up to and including resid via KMT.
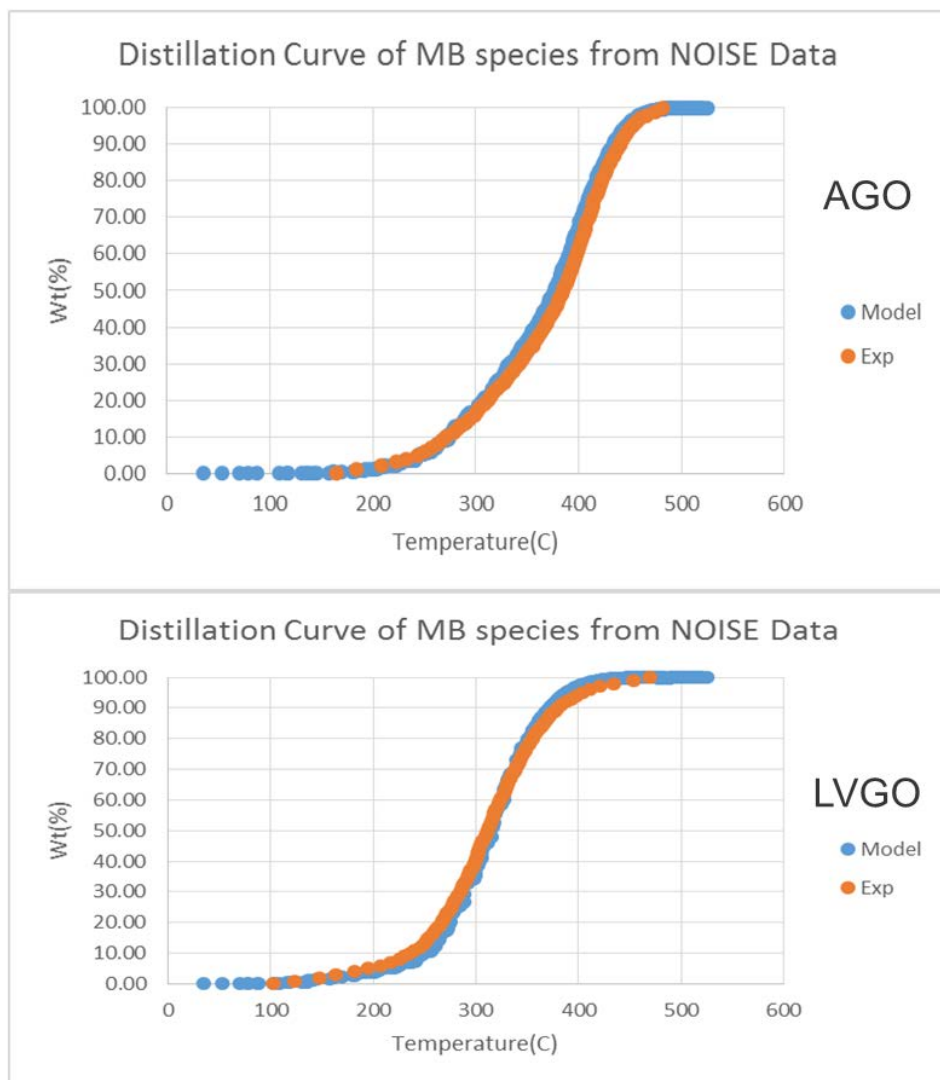
Figure 10. The consistency of species between MB and NOISE data

As a result, the MB HCR/HTR includes thousands of species and reactions that can support the petroleum fraction up to resid. As it is infeasible to tune the parameters of each distinct reaction individually, we apply a Linear Free Energy Relationship (LFER) to thousands of reactions by O (30) parameters.[8,9,10,11] This is practical for users to handle. The parameters in the LFER are strongly associated with the catalyst but independent of individual species and reactions.

To model heterogeneous catalytic reactions (e.g. HCR, FCC, Reformer), the LHHW* rate law was applied in MB equation oriented reactor (EORXR).

Using the MB EORXR model builder, we can automatically convert >5700 reactions and >2400 species into computer code and apply the kinetics and rate law mentioned above. As a result, an MB HCR model block was generated, which can be launched in equation oriented solver engine and integrated into Aspen HYSYS®.

8   "Linear Free Relationships in Heterogeneous Catalysis 1. Dealkylation of Alkylbenzenes on Cracking Catalysts." Isao Mochida and Yukio Yoneda. *Journal of Catalysis*. April 1967, 386-392.

9   "Linear Free Energy Relationships in Heterogeneous Catalysis: II. Dealkylation and Isomerization Reactions on Various Solid Acid Catalysts." Isao Mochida and Yukio Yoneda. *Journal of Catalysis*. April 1967, 393-396.

10   *Molecular Modeling in Heavy Hydrocarbon Conversions*. M.T Klein et al. 2005.
     * Langmuir-Hinshelwood-Hougen-Watson

11   "Vacuum Gas Oil Hydrocracking on NiMo/USY Zeolite Catalysts. Experimental Study and Kinetic Modeling." Tao Zhang et al. *Industrial & Engineering Chemistry Research*. 54.3 (2015): 858-868.

Table 1. Z-CN Matrix Representation of the Feedstock, wt % (NOISE Analysis) [a]

C no	saturates				MAR			DAR		TAR	total
	$Z_{:+2}$	Z_0	$Z_{:-2}$	$Z_{:-4}$	$Z_{:-6}$	$Z_{:-8}$	$Z_{:-10}$	$Z_{:-12}$	$Z_{:-14}$	$Z_{:-18}$	
C5	0.08	0	0	0	0	0	0	0	0	0	0.08
C6	0.6	0.5	0	0	0.01	0	0	0	0	0	1.11
C7	1.11	1.95	0.03	0	0.14	0	0	0	0	0	3.23
C8	1.69	3.24	0.12	0	0.41	0.02	0	0	0	0	5.48
C9	1.92	4.58	0.71	0	0.5	0.13	0	0	0	0	7.84
C10	1.86	3.74	1.39	0.02	0.45	0.32	0	0	0	0	7.78
C11	1.61	2.92	2.54	0.14	0.34	0.49	0	0.01	0	0	8.05
C12	1.34	2.23	3.34	0.44	0.33	0.53	0.03	0.01	0	0	8.25
C13	1.53	2.12	4.08	0.87	0.39	0.47	0.06	0.02	0.01	0	9.55
C14	1.48	1.84	3.45	1.34	0.42	0.41	0.15	0.02	0.03	0.01	9.15
C15	1.36	1.63	2.78	1.64	0.46	0.36	0.29	0.03	0.05	0	8.6
C16	1.2	1.47	2.07	1.7	0.48	0.33	0.35	0.05	0.06	0	7.71
C17	0.92	1.2	1.58	1.35	0.47	0.31	0.31	0.07	0.05	0	6.26
C18	0.95	1.09	1.36	1.12	0.44	0.22	0.24	0.08	0.04	0	5.54
C19	0.82	0.85	1.07	0.82	0.37	0.15	0.15	0.07	0.03	0	4.33
C20	0.55	0.59	0.76	0.53	0.25	0.1	0.1	0.05	0.01	0	2.94
C21	0.26	0.36	0.47	0.34	0.19	0.06	0.06	0.03	0.01	0	1.78
C22	0.14	0.22	0.28	0.21	0.11	0.03	0.04	0.02	0	0	1.05
C23	0.07	0.13	0.15	0.14	0.07	0.02	0.02	0.01	0	0	0.61
C24	0.05	0.07	0.1	0.09	0.03	0.01	0.01	0	0	0	0.36
C25	0.03	0.04	0.05	0.05	0.02	0	0	0	0	0	0.19
total	19.57	30.77	26.33	10.8	5.88	3.96	1.81	0.47	0.29	0.01	99.89

Table 7. Detailed Compound or Class Type Distribution (wt %) of Hydrocracked Products of Run 7 for Catalyst 1 using the Robinson Method

C no.	saturates				MAR			DAR		TAR	total
	$Z_{:+2}$	Z_0	$Z_{:-2}$	$Z_{:-4}$	$Z_{:-6}$	$Z_{:-8}$	$Z_{:-10}$	$Z_{:-12}$	$Z_{:-14}$	$Z_{:-18}$	
C3	2.220	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	2.220
C4	1.321	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.321
C5	2.267	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	2.267
C6	2.414	1.571	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000	3.987
C7	1.818	3.611	0.000	0.000	0.325	0.000	0.000	0.000	0.000	0.000	5.754
C8	2.858	5.439	0.234	0.000	0.770	0.000	0.000	0.000	0.000	0.000	9.302
C9	2.435	5.848	0.889	0.000	0.851	0.000	0.000	0.000	0.000	0.000	10.023
C10	1.830	4.468	1.682	0.023	0.654	0.879	0.000	0.000	0.000	0.000	9.537
C11	1.751	3.364	2.777	0.155	0.462	0.988	0.000	0.000	0.000	0.000	9.497
C12	1.796	2.027	2.976	0.377	0.416	0.785	0.000	0.029	0.000	0.000	8.406
C13	1.426	1.962	3.766	0.780	0.508	0.520	0.082	0.047	0.008	0.000	9.100
C14	1.225	1.529	2.865	1.068	0.381	0.313	0.154	0.032	0.021	0.008	7.597
C15	1.098	1.319	2.257	1.240	0.348	0.219	0.237	0.061	0.045	0.000	6.824
C16	0.865	1.020	1.468	1.140	0.308	0.155	0.186	0.065	0.077	0.000	5.285
C17	0.575	0.721	0.948	0.782	0.239	0.098	0.111	0.058	0.062	0.000	3.593
C18	0.554	0.577	0.769	0.623	0.226	0.049	0.067	0.047	0.043	0.000	2.954
C19	0.304	0.286	0.380	0.287	0.085	0.019	0.023	0.033	0.018	0.000	1.434
C20	0.134	0.120	0.168	0.121	0.044	0.007	0.009	0.005	0.004	0.000	0.611
C21	0.039	0.044	0.059	0.046	0.020	0.002	0.003	0.002	0.002	0.000	0.217
C22	0.005	0.006	0.008	0.006	0.002	0.000	0.000	0.000	0.000	0.000	0.028
C23	0.005	0.011	0.012	0.011	0.004	0.000	0.000	0.000	0.000	0.000	0.044
Total	25.906	34.958	21.257	6.661	5.646	4.034	0.871	0.379	0.279	0.008	100.000

Figure 11. A detailed measurement of feed and product for a hydrocracker case

Figure 12. Detailed calibration results for a hydrocracker case

A case study for hydrocracking using MB EORXR

For this case, we obtain the detailed data analysis for both feed and product shown in Figure 11. [12] We can use the detailed measurement data to calibrate. Figure 12 shows the calibration results as parity plots.
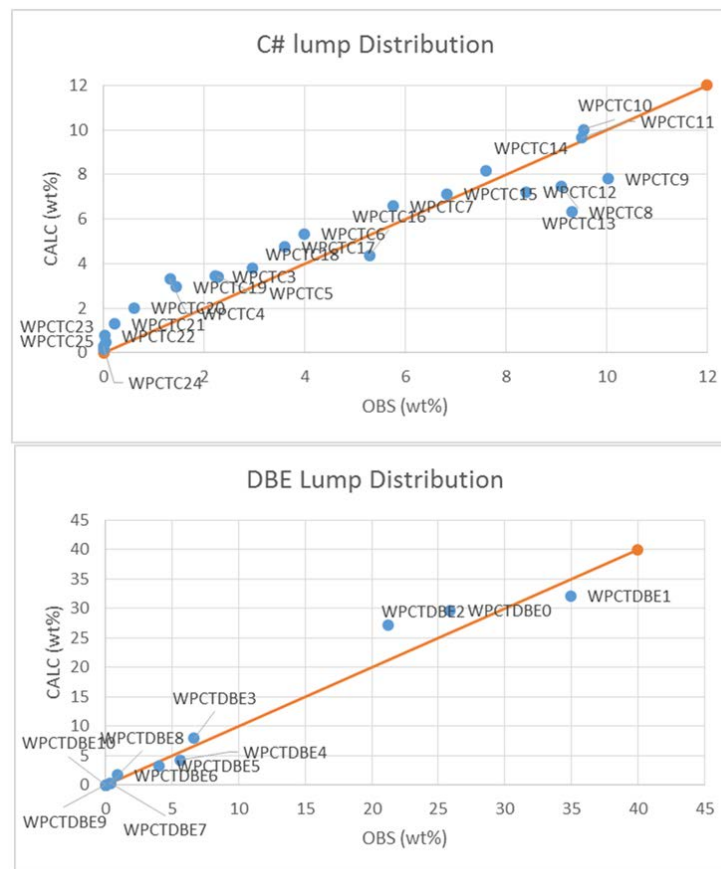
Figure 12 shows that the predicted data is in good agreement with the experimental data at the molecular level, which validates that the MB HCR model can allow users to simulate/calibrate a hydrocracker at the molecular level. In addition to the routine properties reactor models (e.g. density, distillation curve, etc.) provide, the MB HCR model can give users more predictive results in terms of molecular details shown in Figure 13 and thus help users obtain insight into the reactor process.

12   "Vacuum Gas Oil Hydrocracking on NiMo/USY Zeolite Catalysts. Experimental Study and Kinetic Modeling." Tao Zhang et al. *Industrial & Engineering Chemistry Research*. 54.3 (2015): 858-868.
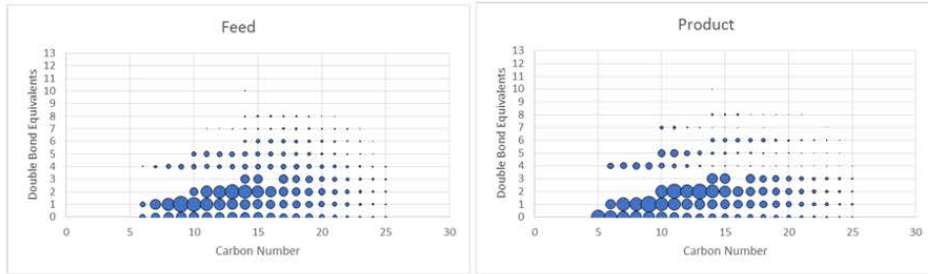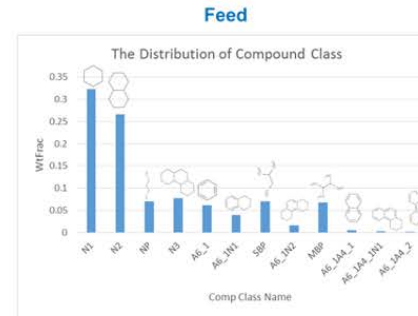
From feed to product

Intensity of data in the area of high C# and DBE # is decreased

Intensity of data in the area of low C# and DBE # is increased

	Feed	Product
n Par wt%	7.0	20.2
iso Par wt%	13.7	2.7
Naphthenes wt%	66.6	67.3
Aromatics wt%	12.6	9.8
Mono-Aromatics wt%	11.8	9.2
Di-Aromatics wt%	0.8	0.6
Tri-Aromatics wt%	0.0	0.0
Poly-Aromatics wt%	0.0	0.0
Carbon wt%	86.3	86.2
C_N wt%	39.2	41.6
C_A wt%	5.1	5.4
Hydrogen wt%	13.7	13.8
TBP 10%,K	413.2	377.6
TBP 30%,K	480.4	455.1
TBP 50%,K	521.4	498.2
TBP 70%,K	562.2	541.4
TBP 90%,K	604.6	592.3

From feed to product

The amount of aromatic compounds were decreased

The amount of Iso paraffin (SBP and MBP) were decreased

The amount of normal paraffin (NP) were increased – cracked more small paraffinic molecules
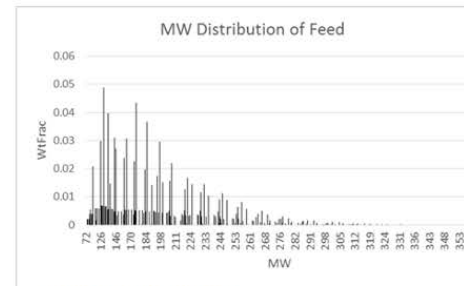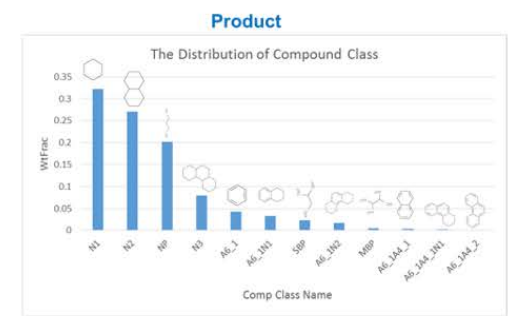
From feed to product

Intensity of data in the area of high molecular weight is decreased

Intensity of data in the area of low molecular weight is increased
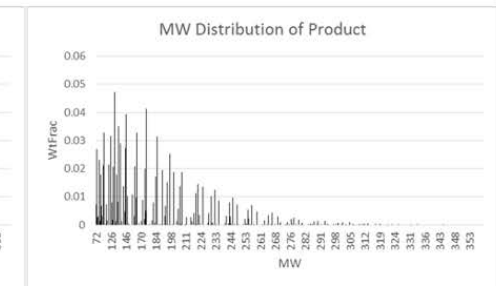
Figure 13. Predictive detailed simulation results of an MB HCR model

In order to use the MB reactor for a complex flowsheet, we developed a technique to allow the molecular information to propagate through a wide range of refinery models as shown in Figure 14.
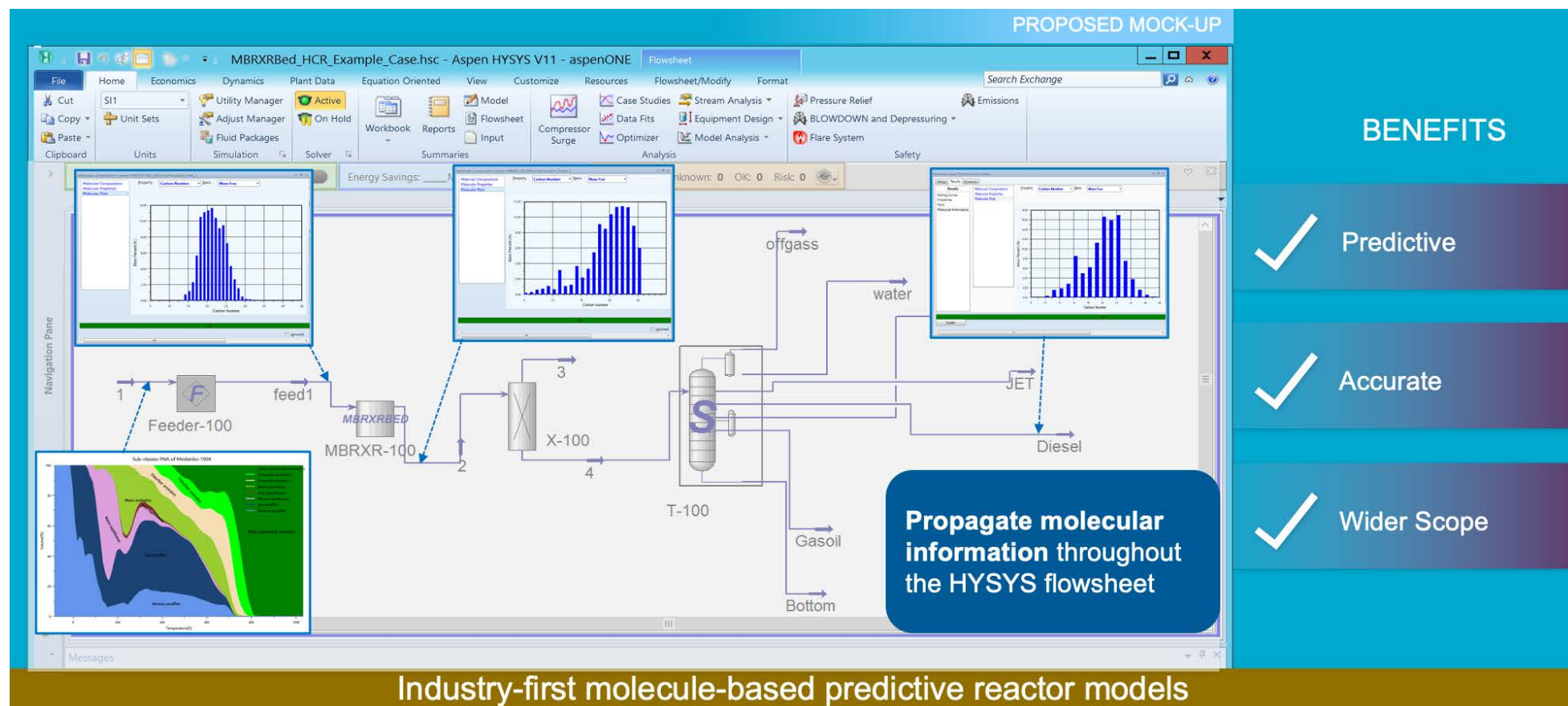
Figure 14. Molecule-based refinery models

Starting from MC, the crude oil measurements can be transferred into the molecule-based composition as a feed stream. The feed's detailed molecular composition will be directly used as the input data of an MB HCR reactor. The MB HCR reactor can give users the molecular composition of a hydrocracker's product streams. Then that molecular information can be propagated through the flowsheet to common Aspen HYSYS unit operations such as flashes, columns, mixers, etc. As a result, users can create and optimize a molecular-level refining flowsheet and take adantage of an opportunity to address the dilemma of integration between refining and petrochemical units in Figure 3.

Using Molecular Modeling to Optimize the Integration of Refining and Petrochemical Processes

Shown in Figure 15, the molecular compositions are characterized by MC first, then passed through a crude distillation unit (CDU). All the product streams of the CDU contain the detailed molecular information and are further upgraded by selected reactors.

For example, the distillate or gas oil can be sent to a hydrocracker. By using an MB HCR model, we can obtain the molecular compositions from the products of a hydrocracker (e.g. HCR naphtha). The mixed stream of HCR naphtha and straight naphtha with molecular compositions can be directly sent as the feed to an ethane cracker or catalytic reformer whose product can serve as the feed of an aromatics production unit. With this molecular refining model, users can calculate the contributions of a naphtha's molecular composition to ethane cracker and aromatics production not only as the feed of those two petrochemical units, but also trace the composition of the feed naphtha to upstream to the crude oil selection, the CDU, the hydrocracker, the reformer and so on. This insight allows users to create an optimization across the refining units and petrochemical units.
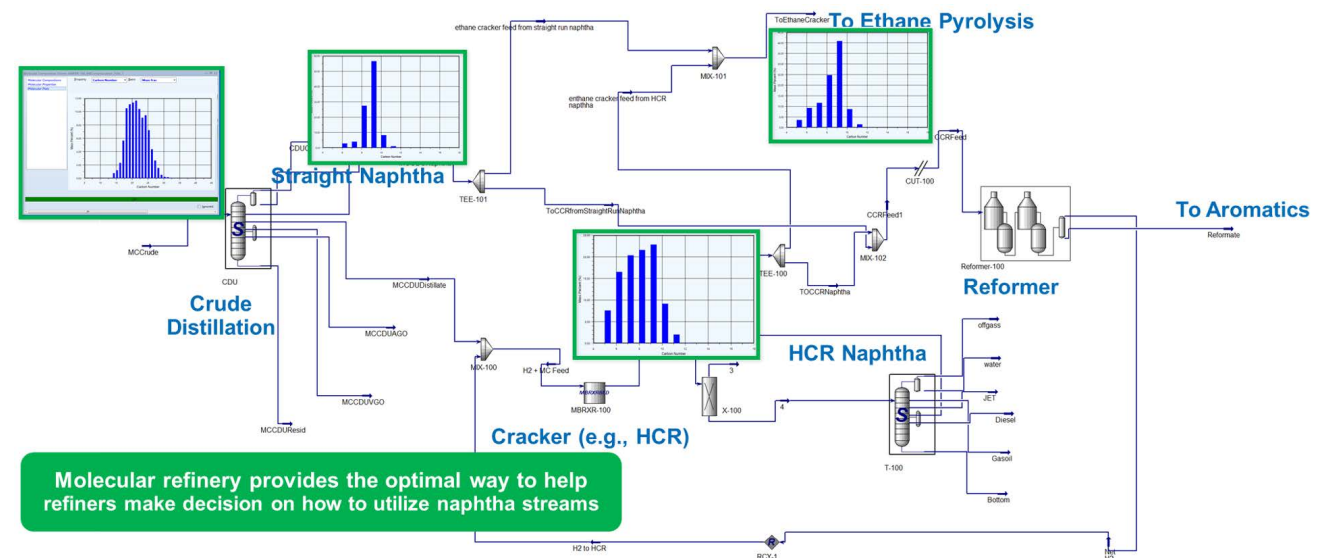
Figure 15. Molecular refinery models for petrochemical integration

In addition to helping users optimize a wide range of units across refining and chemicals plants, molecular modeling can provide the optimal solution through various time scales. Aspen Plus® has the ability to model petrochemical processes (e.g. BTX, ethane cracker, etc.). The MB reactor can seamlessly load refining reactor models into Aspen Plus (shown in Figure 16) to model an MB HCR with petrochemical units together. Users can set up a molecular reactor model in Aspen HYSYS from scratch. After the model is calibrated well, users can load the model into Aspen Plus to perform some advanced operations: set up a steady state model working with petrochemical units and link with Aspen OnLine® to run offline/online process optimization shown in Figure 17.
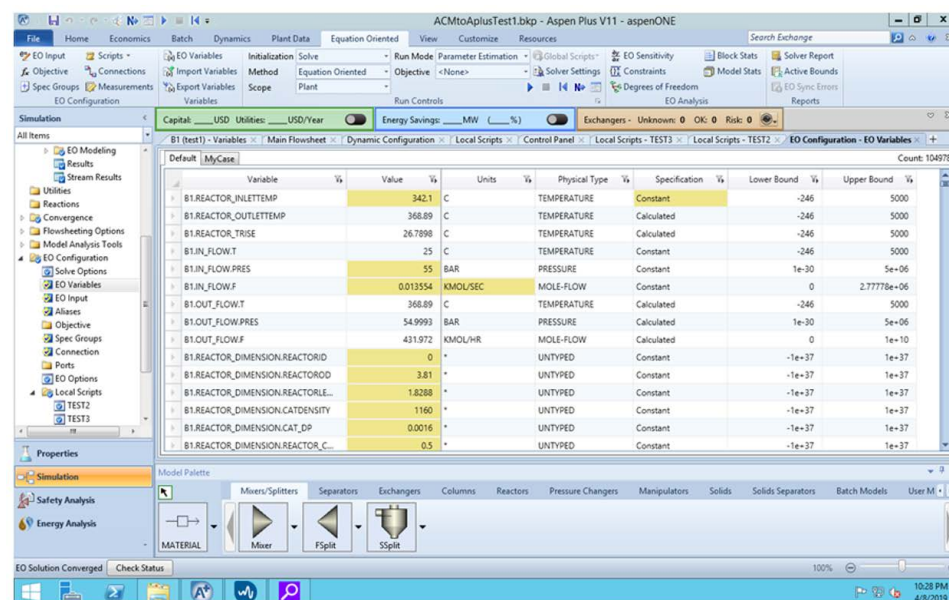
Figure 16. MB HCR reactor model in Aspen Plus
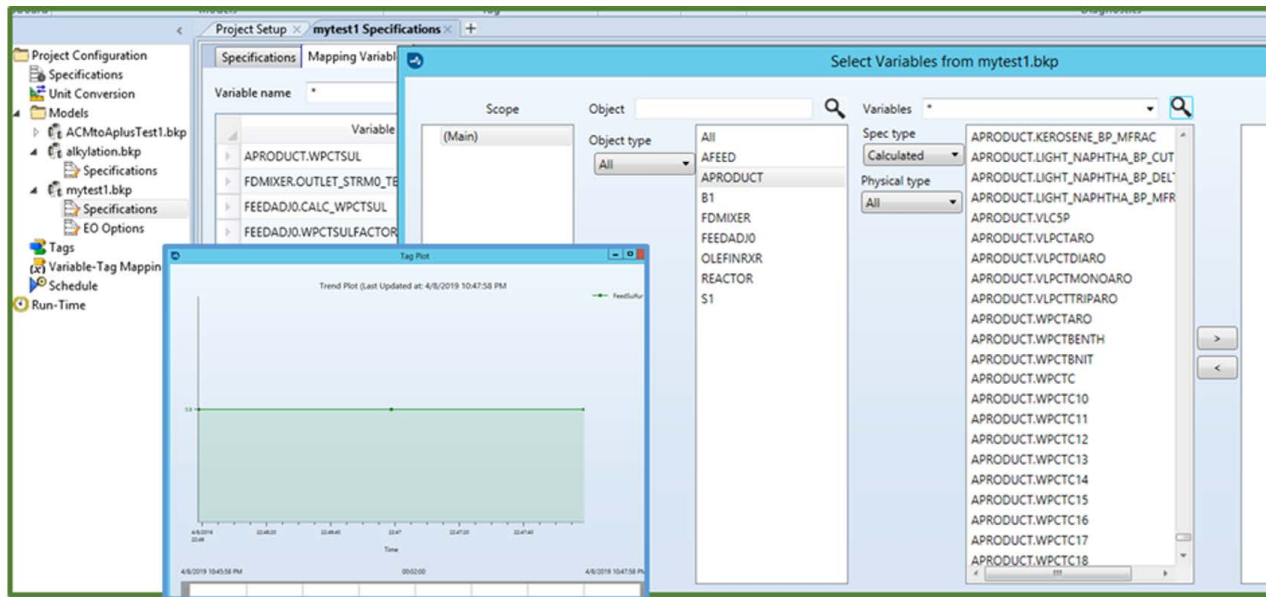
Figure 17. Aspen OnLine to apply the MB HCR reactor model to online open-loop/ close-loop optimization

On the other hand, molecular modeling can give the LP vectors to an Aspen PIMS submodel at the molecular level. For example, a reformer unit in Figure 15 is a key reactor to convert a refining stream to a feed for aromatics production. In the Aspen PIMS model, the submodel of such a reformer needs the feed's detailed molecular information (e.g. detailed PIONA C# break down) in order to work with aromatics model. Without molecular modeling, it is hard for users to propagate the necessary information to the reformer LP sub-model from other units; thus the model is unable to effectively consider the effects of the changes of crude oil to the reformer during the optimization in PIMS.

However, using molecular modeling, any changes on the refining side in Figure 15 (including crude oil) can be seamlessly propagated to the reformer's feed in terms of molecular compositions, providing the needed information to the submodel. If the molecular information is available from the upstream PIMS submodels that feed the reformer, the molecular sub-model of the reformer can be integrated into the PIMS refinery model. The base and delta vectors for molecular reformer model and the upstream models can be generated from the MB reactor models in Aspen HYSYS.

For example, through a set of case studies shown in Figure 18, it is straightforward to generate the base and delta vectors for the submodel of the reformer. Then we can support use of the molecular information directly as the LP vectors in the submodels of PIMS (shown in Figure 19) and allow the refining and chemical models to be optimized together.

Figure 18. Case study of reformer to generate LP vector at the molecular level

Figure 19. Submodel of a reformer in Aspen PIMS at the molecular level

Summary

Molecular modeling is an optimal solution for smart manufacturing in refining at the enterprise level: it addresses multi-scale modeling and optimization across a wider variety of refining and chemical units across one or multiple refineries. Because the molecule is the essential feature in complex hydrocarbon conversions, molecular modeling can use it as a basis to establish the best language system for complex refining process chemistries and provide the foundation to smart manufacturing in refineries.

As shown on the left part of Figure 20, molecular modeling can help users leverage the research results of fundamental science to build industrial process models. As we discussed before, MC and MB reactors can convert the measurements from state-of-the-art analytical chemistries (e.g. FTICR MS/HPLC/NOISE/GC) to molecular compositions using in our process models. The advanced property method (PCSAFT) in MC is derived from statistical thermodynamics and provides the data support for process simulations.

Moreover, we can use the principles of chemistry directly in MB reactors. For example, the classic principles of the Polanyi correlation, and detailed expressions of the adsorption factors of catalysts are used to constrain and set up the kinetics and LHHW rate laws in the reactor model. The simulations and property calculations from quantum chemistry are used to help the MB HCR reactor determine the detailed HDS paths and limit the number of molecular species to a practical level. Molecular modeling can be used as a platform for a refiner's R&D center to set up a "smart research center" to use their academic knowledge base and convert it to industrial process models: build the library of molecular compositions for crude oils, set up the molecular property database, tune the intrinsic kinetic parameters of catalysts and turn them into a quantitative database of catalysts in different processes and deliver the fundamental models for different refining and chemical units.

As shown in the right part of Figure 20, the molecular process models developed from such a "smart research center" can be directly applied to a wide range of refining and chemical units at multi-scale level and thus help users optimize "smart refineries" at the enterprise level. By using the Aspen molecular modeling technique, users can integrate molecular characterizations of crude oils and MB reactors into an entire Aspen HYSYS flowsheet including a wide range of refining and chemicals units. When reactor model claibrations are completed, selected reactor models can be loaded into Aspen Plus and connected with Aspen online for advanced applications: the open-loop/closed-loop online optimization of local refining and chemical units. In addition, the results of molecular modeling in Aspen HYSYS can be applied to support the submodels of Aspen PIMS (e.g. molecular level LP vectors).

Aspen molecular modeling serves as the DNA for refining processes to connect different process units and set up the bridge between fundamental science and industrial applications. It is the foundation of smart manufacturing and asset optimization in refineries.
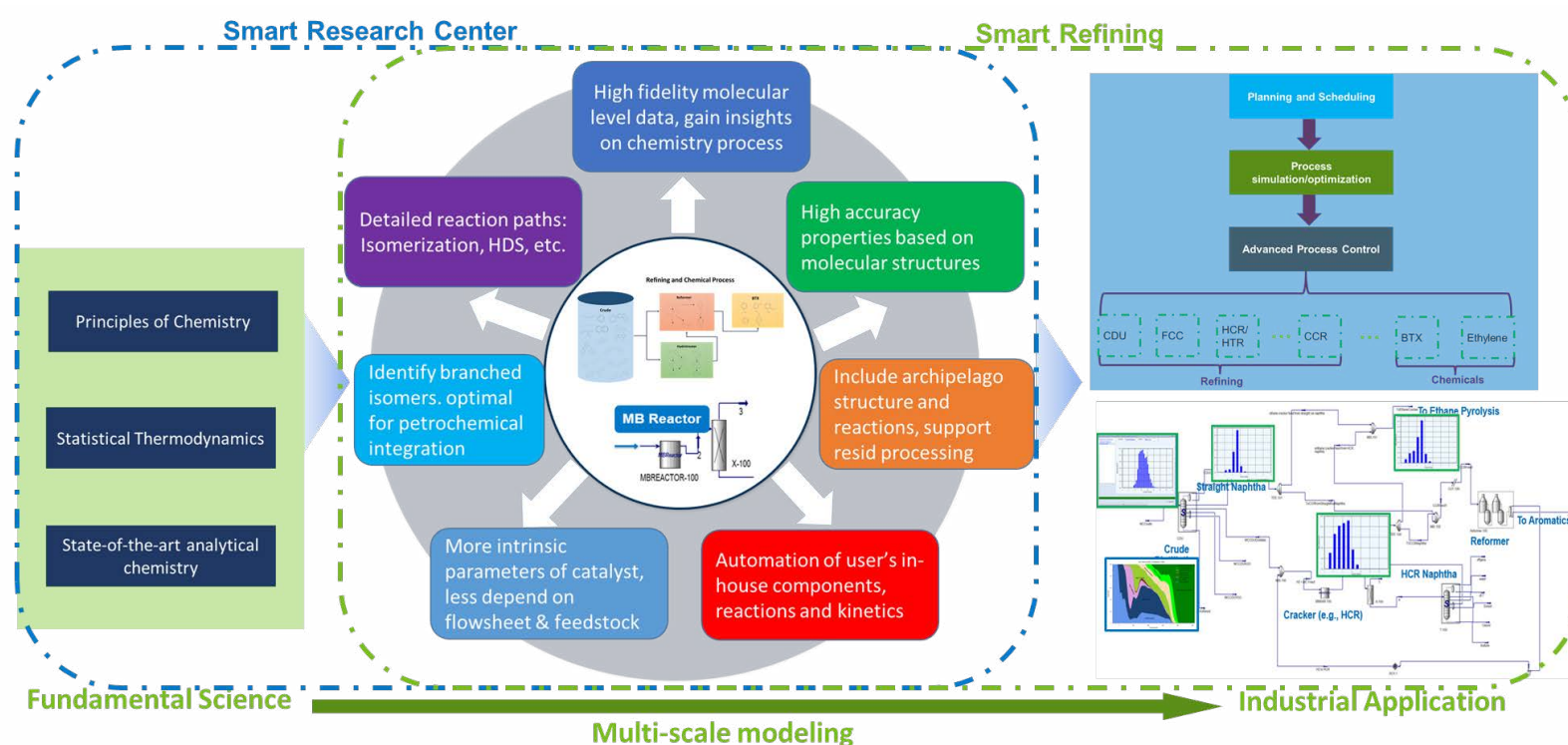

Figure 20. Molecular modeling provides the optimal solution to smart manufacturing

Appendix: Short Overview of Contemporary Research Groups on Molecular Modeling

1. ExxonMobil

ExxonMobil uses a method called structure-oriented lumping (SOL) to describe the composition, reactions and properties of complex hydrocarbon mixtures.[13,14] The basic concept of SOL is that hydrocarbon molecules can be described as a vector, with the elements of the vector representing structural features sufficient to construct any molecule. Each molecule in a mixture is then represented by a structure vector. This approach is still lumping, but at the level of a molecular structure. The structure vector provides a framework to enable rule-based generation of reaction networks and rate equations involving thousands of components and many thousands of reactions. ExxonMobil provides a leading example at the industrial level that shows the large benefits of using molecular modeling across ExxonMobil operations including refining and chemical units.

2. Froment and his coworkers

Froment and his coworkers developed a single-event approach to describe the detailed kinetic models in refining chemistries.[15] They used a Boolean matrix or a vector to represent molecules digitally and derived an algorithm to generate the reaction network. The algorithm was applied to thermal cracking and hydrocracking. The single event approach essentially describes the molecular kinetic models of complex chemistries at a mechanistic level. It is a useful approach for light oil conversion (e.g. reforming, alkylation, methanol to olefin) and model compound studies. However, it requires significant computational resources to apply this approach for conversion processes of heavier feedstocks.

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13 "Structure-oriented Lumping: Describing the Chemistry of Complex Hydrocarbon Mixtures." R.J. Quann and S.B. Jaffe. *Industrial & Engineering Chemistry Research*, 31(11), 2483-2497. November 1, 1992.

14 "Building Useful Models of Complex Reaction Systems in Petroleum Refining." R.J. Quann and S.B. Jaffe. *Chemical Engineering Science*. May 1996.

15 "Single Event Kinetic Modeling of Complex Catalytic Processes." G.F. Froment. *Science and Engineering*. Volume 47, Issue 1. 2005.

3. The Klein Research Group (KRG)

The KRG at the University of Delaware uses the bond-electron (BE) matrix to describe the structure of a molecular species and developed an automated molecule-based kinetic model building toolbox for complex mixtures and chemistries: Kinetic Model Toolkit (KMT).[16,8] KMT includes three main tools (INGen17, CME18 and KME18,19) and a set of auxiliary applications.

KRG represents a molecular component as BE matrix that represents a full 2D atom-explicit structure of a molecule, a radical species or an ion species. Essentially, any chemical reactions can be regarded as bond-making or bond-breaking processes. Therefore, a reaction that transfers the reactants to the products can be described as a matrix operation: the reaction matrix is added to the reactant matrix to calculate the product matrix. This approach was developed as an automated reaction network generation tool called INGen.

The molecular representation of a feedstock is the initial condition for kinetic modeling. CME describes a complex feedstock as a set of homologous series. Each series has a unique molecular structure called a core and is extended by the carbon number extension. Based on the analysis of reactivity information, thermodynamic properties and physical properties, a sub app of CME called HOUGen (Hydrocarbon Oil Universal Generator) was

16   "Computer Generated Pyrolysis Modeling: On-the-fly Generation of Species, Reactions, and Rates." Linda J. Broadbelt, Scott M. Stark and Michael T. Klein. *Industrial & Engineering Chemistry Research*. April 1, 1994. 33.4 (1994): 790-799

17   "User-controlled Kinetic Network Generation with INGen." Craig Allen Bennet. Rutgers, The State University of New Jersey-New Brunswick, 2009.

18   "Software Tools for Molecule-Based Kinetic Modeling of Complex Systems." Zhen Hou. Rutgers, The State University of New Jersey-New Brunswick, 2011.

19   "Computer Aided Kinetic Modeling with KMT and KME." Wei Wei, et al. *Fuel Processing Technology* 89.4 (2008): 350-363

developed to obtain the optimal molecular structures (footprint) of complex feedstocks that range from naphtha to resid.[20] CME describes the mole fractions of the footprint of a feedstock with a set of statistical probability density functions (pdfs) which require just a small number of parameters and employs an optimization loop to minimize an objective function in terms of available analytical measurements. As a result, an optimal molecular representation of a feedstock can be obtained. CME derives the optimal molecular compositions of a feedstock as BE matrices that can be incorporated into kinetic modeling seamlessly.

KME provides a user-friendly VBA interface that allows users to convert complex reaction networks to C code and compile to an executable kinetic model automatically. Users can use the compiled model to run once-through simulation or parameters tuning for research purposes.

KMT provides an automated toolkit to support the development of detailed molecular level kinetic models for academic researchers. AspenTech uses KMT to obtain the detailed species and reaction paths of a complex model and utilizes them to deliver an industrial MB HCR reactor model for general users.

4. University of Manchester

Towler and colleagues at UMIST (University of Manchester Institute of Science and Technology) developed a MTHS (molecular-type homologous series) matrix to represent the molecules in a feedstock and built kinetic models based on this MTHS representation.[21] The MTHS matrix characterization approach represents the composition of a petroleum fraction in terms of homologous series and carbon number information. The matrix framework lumps all the structural isomers of a particular molecular size into one matrix entry. This MTHS matrix is unable to represent the detailed multi-branch paraffins in light end oil conversions. In addition, the molecular structures of polyaromatic hydrocarbon (PAH) and aggregated heteroatom (S, N) rings (>=4) is limited. Therefore, it can be used to build diesel-gasoil range models within its pre-definition of the MTHS, but this MTHS matrix is hard to extend to structures beyond this pre-definition.

20   "Atom-Explicit Composition Models of Heavy Oils." Zhen Hou, Linzhou Zhang, Triveni Billa, Scott Horton and M.T Klein, 8th Symposium on Heavy Petroleum Fractions, 2014.
21   "Molecular Modeling of Petroleum Processes." B. Peng, Ph.D. dissertation, UMIST. 1999.

5. IFPEN

IFP Energies Nouvelles (IFPEN) is a major research and training institute in Europe in the fields of energy, transport and the environment. Starting in the early 2000s, IFPEN developed a method to describe feedstock and kinetic reaction networks at the molecular level. For feedstock characterization at the molecular level, IFPEN proposes a two-step method, SR-REM (statistical reconstruction and reconstruction by entropy maximization). [22,23] IFPEN uses the single event approach discussed above to develop the kinetic and reactor model. IFPEN's limitations are similar to those of Froment's group.

6. China University of Petroleum, Beijing (CUPB)

Derived from ExxonMobil's SOL approach and BE Matrix's idea from KRG, CUPB developed a combined approach called SU-BEM to represent molecular species in hydrocarbon mixtures. [24] A complex molecule is classified as a set of functional structural lumps similar to the SOL method. Each of those complex structures is represented as a bond electron matrix similar to the KRG method. Based on this simplification, CUPB developed a set of tools like KMT to model feed compositions, generate reaction networks, and generate the numerical equations of the models that can be solved via MATLAB.

22   "Molecular Reconstruction of Heavy Petroleum Residue Fractions." J.J. Verstraete, et al. *Chemical Engineering Science*, 65, 304-312. January 2010.

23   "Molecular Reconstruction of Naptha Steam Cracking Feedstocks Based on Commercial Indices." Kevin Van Geen et al. *Computers & Chemical Engineering*, 2007, 31, 1020-1034.

24   "Molecular Composition Modelling of Petroleum Fractions Based on a Hybrid Structural Unit and Bond-electron Matrix (SU-BEM) Framework." Song Feng et al. *Chemical Engineering Science*, 201, 145-156. June 29, 2019.

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