

Risk Mitigation When Implementing New Process Technologies in Refineries and Chemical Plants

Robert P. Absil, Intertek PARC
Pittsburgh, Pennsylvania USA



Technical risks in the biodiesel and oil & refining industries are discussed. Pilot plant testing is considered an independent protection layer to reduce technical risk when implementing new process technologies in refineries and chemical plants.

Several types of risk exist when implementing a new technology in the refining and chemical industries. These include safety risks, financial risks and technical risks. The technical risk is that the technology to be implemented at the plant will not deliver the expected performance as measured, among others, by petroleum coke properties, deasphalted oil metal content or temperature required to make ultra low sulfur diesel (ULSD) sulfur specification. Obviously technical risk is closely tied to safety and financial risks.

Refinery Crude Oil Feedstock Risk:

When considering risk in the refining industry one variable is the feedstock. Conventional crude oil is a complex mixture of hydrocarbon species that boil over a wide range of temperature. The hydrocarbon species include paraffins, cycloparaffins, aromatics, resins and asphaltenes. Crude oil also includes compounds containing heteroatoms, i.e. sulfur, nitrogen, oxygen and metals. The compounds present in the various distillation fractions, such as diesel, vary with crude origin [1]. The complexity of a crude oil or its fractions can be illustrated by considering just the number of

isoparaffins that can exist at a given carbon number. Table 1 shows the boiling points of n-paraffins and the number of isomers that can exist at each carbon number. Similar structural variations also exist for cycloparaffins, aromatics, resins and asphaltenes at a given carbon number.

**Table 1
Number of Isomers as a Function of Carbon Number [2, 3, 4]**

Carbon Number	Boiling of n-Paraffin, deg C	Number of Isomers
5	36	3
8	126	18
10	174	75
12	216	355
15	271	4347
20	343	$3.66 * 10^5$
25		$3.67 * 10^7$
30		$4.11 * 10^9$
35		$4.93 * 10^{11}$
40		$6.24 * 10^{13}$

Due to the complexity of the crude oil, it is difficult to predict the behavior of the fractions in non-catalytic processes, such as deasphalting and delayed coking. While the only variable is the feedstock composition, questions still arise how feedstock will interact with paraffinic solvents in deasphalting or how it will thermally crack in delayed coking and visbreaking operations at process conditions. This increases the risk when implementing new processing technologies in refineries. The risk especially increases when feedstocks quite different from conventional resources are tested. These feedstocks may originate from unconventional resources, such as oil shale, oil sands or biomass. The wide variability in quality across the oil sands reservoir is an issue that needs to be taken into account with bitumen concentration varying considerably vertically and across the reserve [6].

Refining Catalyst Risk:

Another important factor impacting the risk assessment is the nature of the catalysts used in the process. A catalyst is a material that increases the rate of reaction without impacting thermodynamic equilibrium. Two types of catalysts exist: homogeneous and heterogeneous catalysts. Homogeneous catalysts are soluble in the reaction medium, while heterogeneous catalysts are solid catalysts that convert liquid/ gas feedstocks. A comparison of heterogeneous and homogeneous catalysts is provided in the Table 2 [5]. Factors, such as diffusion limitations, poison sensitivity and poor mechanistic understanding, increase the risk when implementing processes employing heterogeneous catalysts.

In the oil & refining industry over 90% of the product will come in contact with solid heterogeneous catalysts [5]. The composition of solid catalyst is complex. The catalyst may consist of several components, such as zeolite, metals and binder. Often the catalyst is dual-functional in that the acidic function, provided by the zeolite, catalyzes cracking and isomerization reactions and the metal function catalyzes hydrogenation reactions, as is the case of hydrocracking catalysts. This, tied to the variability of the composition of the crude oil fractions,

increases the risk of implementing new technologies in refineries. The risk level is especially high when implementing catalytic processes for conversion of substantially heavier crudes, such as shale oil and bitumen.

Catalyst Risk and Biofuels:

In the biodiesel industry vegetable oil, typically sourced from soybeans in the United States, consists of triacylglycerides, also called triglycerides, which are reacted with methanol with a catalyst to produce fatty acid methyl esters (FAME) and glycerol. This reaction is called trans-esterification. The fatty acid methyl esters constitute the biodiesel. The catalyst used in this process is sodium or potassium hydroxide, which is dissolved in the alcohol. The sodium hydroxide is charged as flakes of 99%+ purity; the potassium hydroxide is also charged as flakes but its purity is 90-92% with the remainder being crystalline water [7]. Although based on economics, sodium methoxide solutions can be delivered to the plant, thereby avoiding mixing the hydroxide with the methanol at the plant site [7]. The feedstock is typically soybean oil of high purity. However, other oils and greases contain free fatty acids. These free fatty acids can be troublesome at higher concentrations since they react with sodium hydroxide and form soap and water via saponification, leading to catalyst consumption. High free fatty acid content requires an acid-catalyzed esterification pretreatment step [8]. Comparison of the properties of the sodium hydroxide catalyst to the list in Table 2, show that these catalysts are consistent with those of homogeneous catalysts. They are in the same phase as the reaction medium. Further, the catalyst chemical composition and structure are known and the reaction mechanism is well understood. Consequently, the risk when implementing this technology is substantially reduced.

Start-up companies in the biofuels industry in particular have to deal with higher levels of risk, since programs, which test new concepts in catalysis or process quite different feedstocks, are often initiated without extensive data and rapid initial testing is needed to quickly explore the potential of these concepts. Feedstocks being tested are often bio-mass sourced and have substantially different compositions than conventional crude oils, such as higher oxygen contents and higher total acid numbers [1, 9]. Additional risk is introduced, for example, as heterogeneous catalysts are developed that can simultaneously esterify the free fatty acids and trans-esterify the triglycerides.

**Table 2
Comparison of Heterogeneous and Homogeneous Catalysts [5]**

Heterogeneous Catalysts	Homogeneous Catalysts
Usually distinct solid phase	Same phase as reaction medium
Readily separated	Often difficult to separate
Readily regenerated and recycled	Expensive and difficult to recycle
Rates not usually as fast as homogeneous	Often very high rates
May be diffusion controlled	Not diffusion controlled
Quite sensitive to poisons	Usually robust to poisons
Lower selectivity	High selectivity
Long service life	Short service life
Often high-energy process	Often takes place under mild conditions
Poor mechanistic understanding	Often mechanism well understood

Risk Assessment in ULSD Production:

Consider a refiner deciding to implement Ultra Low Sulfur diesel technology in his refinery. A simple technical risk assessment has been done in Table 3. The refiner or plant operator in the general case has to systematically ask himself what the risks are and whether he can accept these risks. The main risks are whether the refiner will be able to produce ultra low sulfur diesel that meets ATSM specifications using the technologies available on the market.

Risk Management in Process Plant Safety:

The concept of risk and the various means of managing risk are well developed in the field of process plant safety. In the design of operating units, the well known “Hazard and Operability” (HAZOP) and “What-If” studies are performed to assess the safety of unit designs or changes to units. These studies examine 100% of the potential event outcomes, but are however purely qualitative. For example, a HAZOP study may indicate that a relief valve must be installed to prevent tank overpressure and tank rupture [10].

Simplified-quantitative methods use relative rankings of hazards to evaluate the hazard potential of installations or changes to installations. These include the Chemical Exposure Index (CEI) and the Fire & Explosion Index (F&E). The CEI would provide a relative hazard ranking in case the tank ruptured and released its content into the atmosphere compared to releases of other chemicals [10, 11, 12]. Moreover, Layer of Protection Analysis (LOPA) would identify independent layers of protection that would reduce the risk over tank overpressure. An independent protection layer (IPL) is defined as [10]:

“...a device, system, or action that is capable of preventing a scenario from proceeding to its undesired consequence independent of the initiating event or the action of any other layer of protection associated with the scenario.”

**Table 3
Ultra Low Sulfur Diesel HDT Program: Risk Assessment**

Input Variables	Output Variables	Risk Assessment
Feed Rate (bbl/day)	Product Rate (bbl/day) Material Balance (wt %)	
H2 Make Up Rate (scf/bbl)	H2 Bleed Rate (scf/bbl)	What is the Impact on Performance? Can H2 be Supplied?
Inlet H2 Composition (vol%) H2 Recycle Rate (scf/bbl)	H2 Tower Rate (scf/bbl) H2 Consumption (scf/bbl)	
Inlet Pressure (psig)	Outlet Pressure (Psig) Pressure Drop (psig/L)	Is Pump Capacity Correct?
Temperature, F		What Is the Cycle Length? Can Catalyst Be Regenerated?
Catalyst		Has Optimal Catalyst Been Selected?
Reactor Dimensions (L/D) Liquid Distributor Configuration		What Is Catalyst Contacting Efficiency?
Reactor/ Tower Integrity		Is Vessel Rated for Operating Pressure? Is Equipment Integrity Status Known?
Feed Composition API, D-482 Sulfur, D-5453 Distillation, D-86	Product Composition API, D-482 Flash Point D-93 Sulfur, D-5453 Distillation D-86 Kinematic Viscosity D-445 Ash, D-482 Water & Sediment D-2709 Copper Strip Corrosion, D-130 Cetane Number, D-613 Cetane Index, D-976 Aromativity, D-1319 Cloud Point, D-2500 Ramsbottom Carbon, D-524 Lubricity, D-6079 Conductivity, D-2624, 4308	Can Specification Be Met? Can Specification Be Met? Can Specification Be Met? Can Specification Be Met? Can Specification Be Met? Can Specification Be Met? Can Specification Be Met? Can Specification Be Met? Can Specification Be Met? Can Specification Be Met? Can Specification Be Met? Can Specification Be Met? Can Specification Be Met? Can Specification Be Met? Can Specification Be Met? Can Specification Be Met?

Examples of IPLs include relief valves, which prevent the system exceeding specified overpressure. The PFD for a relief valve is for example 1 out of 100. Thus by installing a relief valve the risk of overpressure is reduced by a factor of 10^{-2} . LOPA is also semi-quantitative and assigns orders of magnitude to probabilities of failure on demand (PFD) of independent layers of protection. LOPA can be used in any stage in process development, but is most frequently used in the design stage when piping and instrumentation diagrams are complete. LOPA is used to examine scenarios generated by qualitative process hazard tools (HAZOP, what-if, etc.) when the consequences are not clear, the frequency of the final consequences is not known or when processes are too complex to address qualitatively. LOPA, CEI and F&EI are applied to 10-20% of the scenarios considered in a HAZOP analysis [10].

Full quantitative risk analysis (CPQRA) is applied to a small percentage (1%) of the potential situations. This analysis is used to help evaluate potential risks when qualitative methods cannot provide adequate understanding of the risks and more information is needed. Quantitative risk analysis includes statistical and probabilistic modeling of frequency and consequence of a single scenario. Thus in case of tank rupture and release of its content, CPQRA would determine the number of fatalities at a distance of say 1000 meter away from the unit and the frequency of this occurrence [10, 13].

Independent Protection Layer Applied to the Refining Industry:

Let's revisit the refiner who wants to implement ULSD process technology. After examining the output variables and semi-quantifying the level of risk associated with achieving these output variables, he must ask himself what level of risk he is willing to accept. If the level of risk is not acceptable, then one way to reduce the risk of implementing new technology is by adding an independent protection layer (IPL) analogous to what is done in the process plant safety field.

An independent protection layer often used in the refinery and chemical industries is pilot plant testing [14]. A pilot plant is a unit that simulates the operation of a refinery unit except on substantially reduced scale. Pilot plants can cover non-hydroprocessing refinery units, such as a delayed coker, deasphalter and visbreaker. Pilot plants can also simulate operations of fixed bed reactors used in hydrotreating, hydrocracking, reforming and isomerization. Micro-reactor testing is primarily used for initial screening of catalysts, but bench and pilot plant reactor are used for confirmation of catalyst performance and product specifications. In the present case of implementing new ULSD hydrotreating technology, the independent protection layer would be independent third-party pilot plant testing or bench reactor testing services. It would be able to provide data on temperature requirements, cycle length and product specifications.

Independent testing means that confidential testing services are provided by the company whose only revenues are from the pilot plant services provided. The testing company does not compete with its clients nor owns technology that it markets itself. An additional advantage is that the company providing the testing services has extensive experience which can facilitate program execution. A further advantage is that while a client may have pilot plant facilities of his own, common cause failure may warrant that testing be done by an independent company. While this is a complex issue, it may pay in the long run to do independent testing prior to implementing complex technology in the refinery.

The level of risk can be mitigated by experience. Databases and complex models can be developed that correlate catalyst performance. Instead of focusing on individual compounds, groups or "lumps" of compounds that fall into similar chemical classifications have been used with

success [4]. In even deeper analysis, the surfaces of catalysts can be characterized and its properties can be correlated to catalyst performance. These give confidence of process performance and reduce the risk of implementing the technology in the refinery or in a chemical plant.

Intertek PARC as an Independent Protection Layer:

Intertek PARC has been providing independent pilot plant testing services to the global oil & refining industry since 1986. It meets the criteria of an independent protection layer and can and has continued to act as an independent protection layer to the oil & refining and biofuels industries to mitigate the risks when implementing new technologies in refineries or process plants.

References:

1. Speight, J.G., and Ozum, B., Petroleum Refinery Processes, Marcel Dekker, Inc., New York, 2002.
2. Solomons, T.W.G., Organic Chemistry, John Wiley & Sons, Inc., New York, 1976, pp. 96.
3. Altgelt, K.H., and Boduzynski, M.M., Composition and Analysis of Heavy Petroleum Fractions, Marcel Dekker, New York, 1993 (cited by [4]).
4. Lynch, T.R., Process Chemistry of Lubricant Base Stocks, CRC Press, New York, 2008, pp. 12-13.
5. Lancaster, M., Green Chemistry, The Royal Society of Chemistry, TJ International Ltd, Padstow, Great Britain, 2002, p. 87.
6. Fustic, M., et al... 2006 CSPG-CSEG-CWLS Convention, pp. 640-652.
7. Markowitz, M., www.biodiesel magazine.com/article-print.jsp? article_id=462, May/June 2004, retrieved 7/27/2010.
8. Drapcho, C.M., Nghiem Phu Nhuan, Walker, T.H., Biofuels Engineering Process Technology, The McGraw-Hill Companies, New York, 2008, Chapter 6, pp. 197-262.
9. Casmaa, A., Peacocke, C., A Guide to Physical Characterisation of Biomass-derived Fast Pyrolysis Liquids, Espoo 2001, Technical Research Center of Finland, VTT Publications 450.
10. AIChE, Layer of Protection Analysis, Center for Chemical Process Safety, AIChE, New York, 2001.
11. AIChE, Dow's Chemical Exposure Index Guide, AIChE, New York, 1994.
12. AIChE, Dow's Fire & Explosion Index Hazard Classification Guide, AIChE, New York, 1994.
13. AIChE, Guidelines for Chemical Process Quantitative Risk Analysis, AIChE, New York, 2000.
14. Absil, R. P., "Pilot Plant Testing: Risk Minimization in Refinery Process Implementation," Intertek Trends in Energy Conference 2010, Houston, Texas, July 21, 2010; <http://www.intertek.com/trends-in-energy-conference/>