FLOWSHEET OPTIMIZATION OF A LUBRICANT BASE OIL HYDROTREATMENT PROCESS

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Abstract - Unsaturated, nitrogenated and sulfured compounds may reach undesirable levels in lubricant base oils, requiring hydrotreatment (HDT) at high temperatures and pressures. HDT processes are well known for their high capital and operational costs due to the use of hydrogen, compressors and multistage heterogeneous reactors. Process costs are thus highly dependent on the applied conditions. An oversized process entails unnecessary costs and capital investment. On the other hand, mild reaction conditions lead to unspecified products. This work analyzes the process using a compositional modeling and a kinetic framework developed previously (Barbosa et al., 2002) for the HDT of lubricant base oils. The industrial reactor is rigorously modeled on an adiabatic and multistage configuration. For the remaining equipment in the flowsheet, we adopt shortcut models for compressors and exchangers. The process is then optimized in terms of its variables subject to product specification constraints.
Keywords: lubricant oil, hydrotreatment, compositional modeling, optimization.

INTRODUCTION

Lubricant base oils are a complex mixture of paraffinic, aromatic and naphtenic hydrocarbons with molecular weights ranging from medium to high values, which produce oils with desirable viscosities, densities and distillation curves. However, these oils may have olefinic, nitrogenated and sulfured compound contents that jeopardize the quality of the final product. In order to meet composition specifications, these oils are submitted to the hydrotreatment (HDT) process before addition of other compounds for commercial production. This process – herein referred to as HDT-LUB – is characterized by the use of operational conditions of low or medium severity so that aromatic distribution is not seriously affected and sulfur compounds are

not completely removed, as these compounds affect positively resistance to oxidation under service.

In addition, process costs have nontrivial characteristics associated with: (i) the high value of product and raw material; (ii) mandatory compliance with the product oil composition requirements; (iii) the use of an expensive reactant (hydrogen); (iv) operation at high temperatures and pressures; (v) need for investing heavily in compressors and specific heterogeneous catalysts.

This discussion is important in establishing that observation of operational conditions near an optimal point is a critical factor in HDT-LUB profitability. Problems in obtaining an optimum process include the description of: (i) composition of base oil which, like other crude oil fractions, has a complex structure; (ii) reactive process involving heterogeneous

catalytic reaction networks; (iii) adiabatical operation of the industrial reactor in various hydrogenation stages, under medium and high pressure conditions, multiple hydrogen feeds and with liquid and vapor phases in constant equilibrium; and (iv) the overall process including, in addition to the reactor, peripheral structures for feed preheating, heat recovery, compression and hydrogen recycling.

This paper analyzes HDT-LUB, aiming to optimize the process and operational aspects under the constraints of product specifications. Previously developed compositional modeling (Barbosa et al., 2002), based on feed and product characterization data in a pilot plant (Valle et al., 1998), is used for the base oil and reaction network.

HDT-LUB is approached on three levels:

(i) development of a steady state simulator to predict the final state of the product and hydrogen and utilities consumption from process variables; (ii) definition of the economic objective, taking into account realistic aspects of process costs and the need to achieve product specification; and (iii) optimization of design and operation.

The process was modeled rigorously on an industrial reactor, formed of several adiabatic stages with liquid and vapor phases in constant equilibrium. Adiabatic separation vessels and the recycling structure were also modeled rigorously. The rest of the process was modeled using simple compressor, heat exchanger, scrubber and furnace models (Douglas, 1988). Investment was modeled according to Guthrie´s proposition (Douglas, 1988).
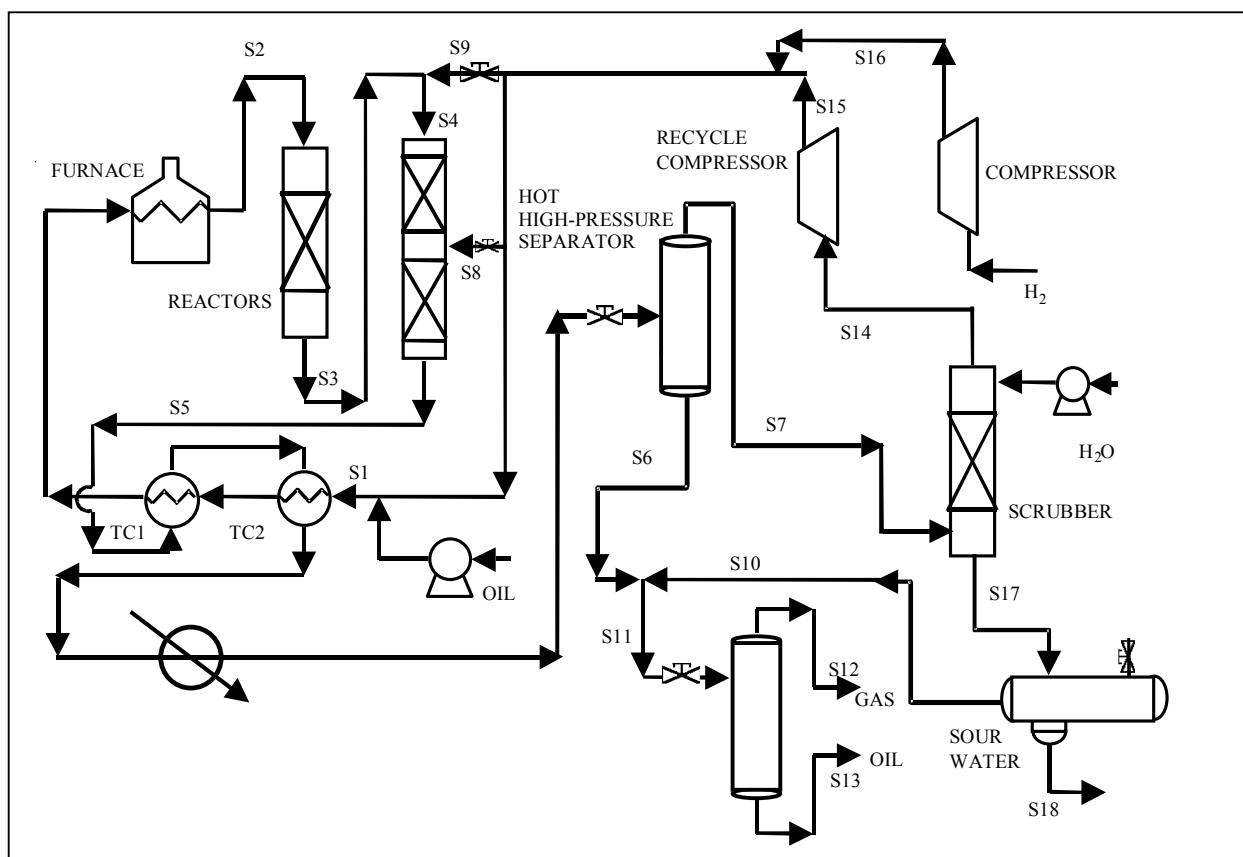

Figure 1: HDT Process Flowsheet.

THE HDT-LUB PROCESS

The HDT process is shown in Figure 1. A fixed base oil feed of 25000 kg/h, pumped and mixed with hydrogen under pressure, is assumed. The feed is preheated by a reactor outlet stream and then is

heated to the reactor inlet temperature in the furnace. HDT takes place in a fixed bed with multiple gas recycle injections to supply hydrogen and control reaction temperature. After leaving the reactor and losing heat in the next water-refrigerated heat exchanger, the mixture is depressurized and

separated from hydrogen in a high-pressure separator. The gas generated is sent to a water scrubber for hydrocarbon, H_2S and NH_3 retention. The recycle compressor pumps the recycle gas obtained at the top of the scrubber. The oil at the bottom of the high-pressure separator is expanded in the low-pressure separator, producing residual gas and treated oil. Key variables, which have decisive roles in the process performance, are the following:

1) Temperature at the furnace exit ($T_{FURNACE}$). Its increase favors high rates of HDT reaction, although one has to consider the impact on furnace costs and the highly exothermic characteristics of HDT reactions, which increase the possibility of generating elevated thermal levels at some point in the reactor. Also, some exothermic equilibrium reactions, such as hydrogenation of tri- and tetra-aromatics, are shifted unfavorably with an increase in reactor temperatures.

2) Feed pressure at reaction stage 1 ($P_{COMPRESSOR}$). Hydrogen fugacity directly influences the kinetics and severity of the process. Its increase favors all HDT reactions, although it creates investment problems due to feed and recycle compressor design.

3) Reaction stage spatial velocities ($WHSV_1$, $WHSV_2$ and $WHSV_3$). An increase in WHSV (weight hourly spatial velocity) translates into reduction of catalyst mass, reducing the severity of the process and investments. WHSV reduction can be used to maintain the level of severity as feed pressure is reduced.

4) Hydrogen/feed ratios $RH2HC_1$, $RH2HC_2$ and $RH2HC_3$ in reaction stages. The increase in hydrogen recycling has advantages, such as the quenching effect at injection points, and favors heavy hydrocarbon vaporization, thus helping to maintain thermal control over the reactor. Also, a higher concentration of hydrogen inside the reactor results in easier maintenace of fugacity level, guaranteeing constant reaction rates. Problems that arise are the need for larger compressors and equipment in the recycle loop.

COMPOSITIONAL MODEL AND REACTION NETWORK

Barbosa et al. (2002) characterized lube base oil by data reconciliation, using a compositional model (CM), based on experimental data obtained from Valle et al. (1998). Adjustment of CM parameters is based on making the values of estimated properties equal to experimental data, such as density and distillation curve. These calculations use correlations and thermodynamic models, as well as the Joback group contribution method (Reid et al., 1987). The CM developed by the authors has 23 key components with five different paraffinic side chains. The authors also proposed a reaction network for the HDT-LUB process, with 14 (ncin=14) kinetic laws, 39 (n=39) chemical reactions and 51 (nc=51) chemical species. Kinetic and adsorption parameters for the network were estimated based on pilot plant data obtained by Valle et al. (1998). All results generated by Barbosa et al. (2002) were used in the present paper: (i) CM feed parameters; (ii) the reaction network matrix ($\underline{\underline{H}}$: stoichiometric matrix (nc by nr); $\underline{\underline{S}}$: component selection matrix for reaction rate definition (nr by nc); $\underline{\underline{D}}$: matrix for association of kinetic laws with reactions (nr by ncin); (iii) vector of Arrhenius constants ($\underline{K}(T)$) ((gmol/h)/(kg catalyst . bar)) for kinetic laws (ncin by 1); and (iv) Langmuir constants for adsorption on the catalyst (K_{H2}^*, K_{H2S}^*, K_{NH3}^*, K_{H2O}^*).

HDT-LUB MODELING

The flowsheet shown in Figure 1 was modeled as follows. After solving the equipment equations, their installed costs (ISBL, US$) were determined by the Guthrie models (Douglas, 1988) for year 1988 using the corresponding Marshall-Swift (M&S) index. Annual operational costs (UTIL, US$/year) were defined based on respective consumption of utilities. Table 1 contains the premises adopted:

1) Thermodynamic properties:

2) Fugacities, densities and enthalpies are estimated using cubic equations of state (Soave/Peng-Robinson) and the Joback method (critical constants and ideal gas enthalpies).

3) Liquid-vapor separation via Flash Rigorous Algorithms (P,H) and Flash (P,T): applied to separation vessels, reactor and energy balance in two-phase streams.

4) Heat exchangers: once temperature approximation intervals (ΔT_{AP}) are defined, thermal duty for each stream is calculated (via Flash (P,T)). Limiting stream, heat exchanger duty and final temperatures are determined. Area and ISBL are calculated for constant thermal coefficients (U). Operational costs (UTIL) are calculated only for water-refrigerated exchangers.

5) Reactor: The three adiabatic stages model assumes: (i) liquid-vapor equilibrium in the axial direction; (ii) plug-flow; (iii) stages calculated individually by integration of mass balance equations (Equation 1) associated with isenthalpic liquid-vapor equilibrium for determining temperature profiles.

Table 1: Premises for HDT-LUB

M&S Index (1988): 800
P_{H2}=2.5 US\$/kg, P_{RAW}=0.5US\$/kg
P_{LUB}=0.7 US\$/kg, P_{CAT}=10US\$/kg
Vapor High:11, Medium: 7.5, Low: 6 US\$/ton
Heat: 4 US\$/106 BTU
Water: 0.086 US\$/ton
Feed: 25000 kg/h, T=50°C
Vessel P_{LOW}=1.1 bar
Vessel P_{HIGH}=25 bar
Reactor L/D=10
Compressor: N_S=3, T_I=77C, η=70%
Scrubber: T=40C, Res. Time =110s, L/D=5
Vessel: Res. Time =120s, L/D=3
Exchangers: ΔT_{AP}=45C, U=0.5kW/m^2.C

$$\frac{d}{dt}(\underline{N}) = F_0 \Xi \ \underline{\underline{H}}\left[\underline{\underline{Diag}}\left(\underline{\underline{DK}}(T)\right)\right]\underline{\underline{Sf}} \qquad (1)$$

where

$$\Xi = \left[\frac{\sqrt{K_{H2}^* f_{H2}}}{1+\sqrt{K_{H2}^* f_{H2}} + \Omega}\right]$$

$$\Omega = K_{H2S}^* f_{H2S} + K_{NH3}^* f_{NH3} + K_{H2O}^* f_{H2O}$$

F_0 is the oil feed flow rate (kg/h), t is the spatial time (kg catalyst/(kg/h)) and N is the species rate vector (gmol/h). Equation 1 is integrated into stage k from 0 to 1/WHSVk. Reactor ISBL is determined by the catalyst inventory (catalyst price in Table 1) and the pressure vessel ISBL.

Compressor: Power (BHP) in N_S stages, efficiency η, feed (T_E (K)) and interstage (T_I (K)) temperatures, compression ratio Θ, flow rate Q (gmol/s) and polytropic exponent ($\gamma = C_P/C_V$); Equation 2 follows (R=8.314 J/gmol.K):

$$BHP = \Gamma\left[\Theta^{\frac{\gamma-1}{\gamma.N_S}} - 1\right] \qquad (2)$$

$$\Gamma = \frac{\gamma.R.(T_E + (N_S -1)T_I).Q}{746(\gamma-1)\eta}$$

ISBL is determined with BHP, stipulating a turbine-operated centrifuge compressor. Operational cost corresponds to high-pressure vapor in the turbine.

The process design is generated from eight-variable process vector $\underline{V}$: (i) $P_{COMPRESSOR}$ (bar); (ii) $T_{FURNACE}$ (ºC); (iii) WHSV1, WHSV2 and WHSV3 (kg/h/kg catalyst); and (iv) RH2HC$_1$, RH2HC$_2$ and RH2HC$_3$ (Nl/kg). Search intervals are defined by $\underline{V}_{min}$ and $\underline{V}_{max}$ so that $100 \leq$ RH2HC1 ≤ 400; $50 \leq$ RH2HC$_2$, RH2HC$_3 \leq 400$; $1 \leq$ WHSV$_1$, WHSV$_2$, WHSV$_3 \leq 6$; $300 \leq T_{FURNACE} \leq 350$; and $40 \leq P_{COMPRESSOR} \leq 120$).

ECONOMIC OBJECTIVE

It can be shown that a ten-year process with 12% annual rate of return, negligible labor costs and "instantaneous" implementation, has an annualized profit function (AP, US\$/year) given approximately by Equation 3 (Douglas, 1998):

$$AP = REV - RAW - \sum_k UTIL_k - \sum_k ISBL_k \qquad (3)$$

where $ISBL_k$ and $UTIL_k$ are installed capital (US\$) and annual utilities costs (US\$/year) of unit k and REV and RAW represent annual income and raw material costs (US\$/year). In HDT-LUB these costs are derived from H_2 and fixed-price oil consumption (P_{H2} and P_{RAW}). Income results from product rates

and its market price (P_{PROD}), which has a maximum (P_{LUB}) if specifications are achieved. These constants are shown in Table 1. Equation 4 gives the product price model, where C_k is the kth valid assay for the commercial fitness decision, while $[L_k, U_k]$ represent the acceptable interval for C_k, and β is a large positive constant.

$$P_{PROD} = P_{RAW} + \left(P_{LUBE} - P_{RAW}\right)$$
$$\prod_k \left\{ \frac{1}{1 + \exp\left(\beta\left(L_k - C_k\right)\right) + \exp\left(\beta\left(C_k - U_k\right)\right)} \right\} \qquad (4)$$

This function has the role of eliminating specification constraints from the objective function of the process, so that the values of products that do not agree with $L_k \leq C_k \leq U_k$ for any k depreciate. Specifications used for characterizing commercial oil are listed in Table 2. Equation 5 gives the optimization formulation. Search variables in the unconstrained space θ are defined in Equation 6. The HDT-LUB process was optimized using the SIMPLEX Nelder-Mead method (Reiklaitis et al., 1983), with Equations 5 and 6, in MATLAB R12 environment. Final values obtained were $P_{COMPRESSOR}$ = 40.8 bar, $T_{FURNACE}$ = 328.6 $^{\circ}$C, $\underline{WHSV}$ = [1.66, 3.2, 3.7] h^{-1}, and $\underline{RH2HC}$=[177.8, 213.9, 130] (Nl/kg).

$$\text{Max } AP(\underline{V})$$
$$\underline{V}_{min} \leq \underline{V} \leq \underline{V}_{max} \qquad (5)$$

$$\underline{V}(\theta) = \underline{V}_{min} + (\underline{V}_{max} - \underline{V}_{min}).\left\{ \theta^2 / (1 + \underline{\theta}^2) \right\} \qquad (6)$$
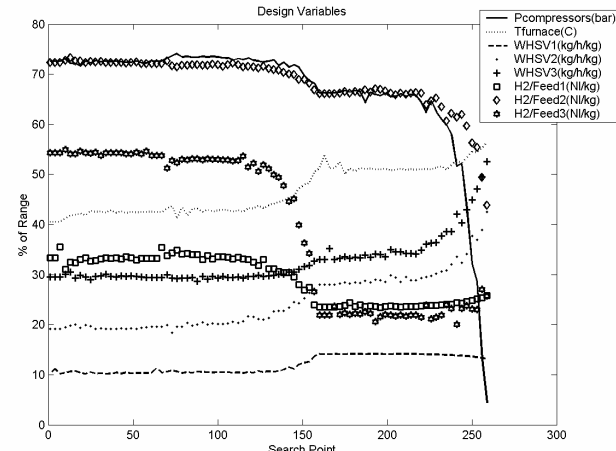
RESULTS

Starting from a viable loosely defined initial condition, trajectory of function AP (Figure 2a) evolves along the feasible region contours, exploring viable and nonviable designs (Figures 2a and 2c). Each nonviable condition found creates a sudden reduction in AP, causing the method to increase severity and thus return to a viable design. The objective value was markedly increased from the initial condition, tightening process operational conditions and obtaining a more economic combination of variables that influence severity. When the search was interrupted near 14 MMUS\$/year, it was sloping up, with 2.6 MMU\$ of total ISBL and 3.8 MMU\$/year for H_2 costs. The search is directed towards lowering operating pressure and reactor size (Figures 2b and 2d), increasing furnace temperature to maintain the necessary severity for meeting the specification. It can be seen that 40ºC viscosity fitness was the main factor that defined the applied severity level (Figure 2f). Results for the optimum design simulation showing some property profiles for the reactor are given in Figure 3. Some reductions such as the following can be highlighted: (i) density; (ii) sulfur and nitrogen contents; (iii) simulated distillation curve temperatures and (iv) effects of the three hydrogen injections on temperature profiles, enthalpy fluxes and fraction vaporized inside the reactor.
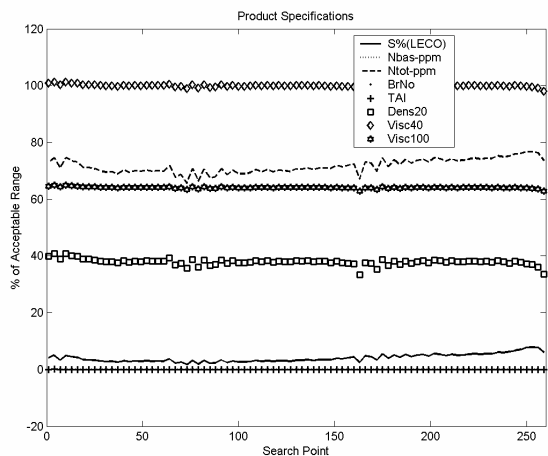
Table 2: Limits of Commercial Fit

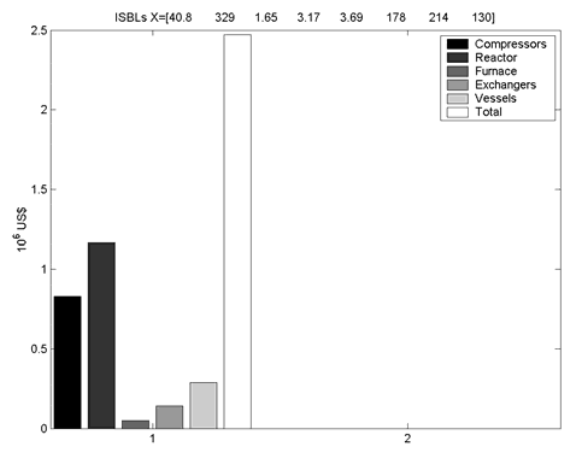| Specification	Range
Viscosity [40C], cStk	[2, 11]
Viscosity [100C], cStk	[1, 5]
Density [20C], g/cm^3	[0.76, 0.88]
Sulfur % (mass)	[0, 0.05]
Mercap. Sulfur, ppm	[0, 100]
Total Nitrogen, ppm	[0, 300]
Basic Nitrogen, ppm	[0, 300]
Bromine Number	[0, 1]
Acidity Index, mgKOH/100g	[0, 1]
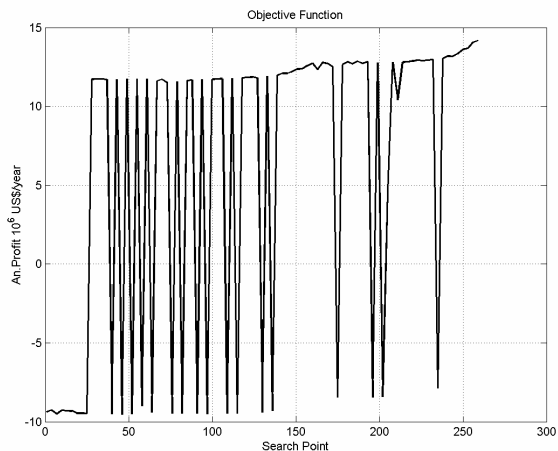
(a)

(b)

(c)
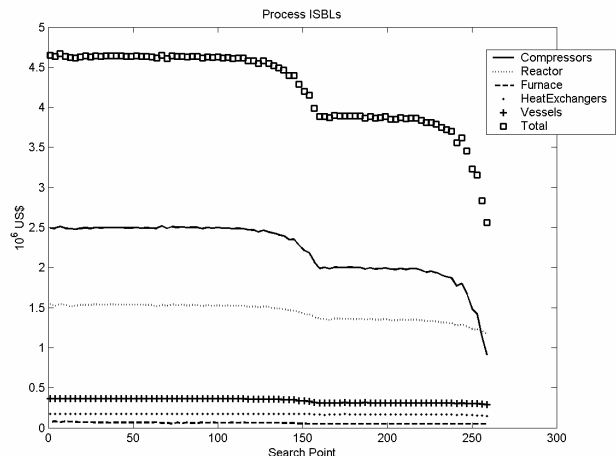
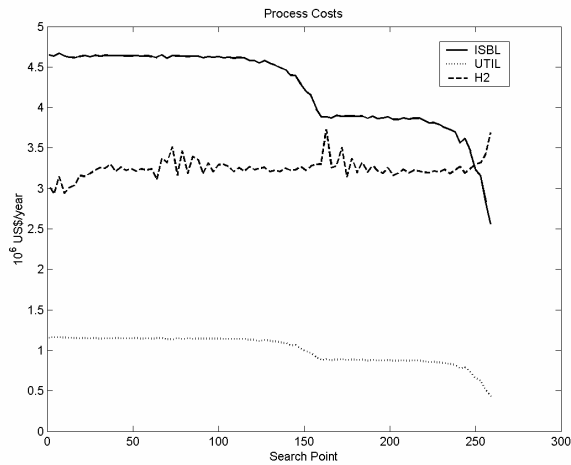(d)
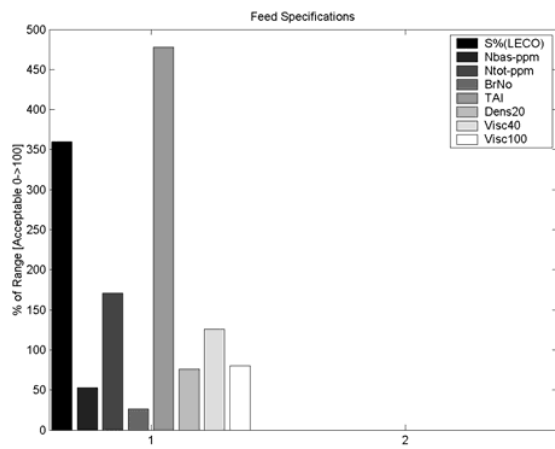
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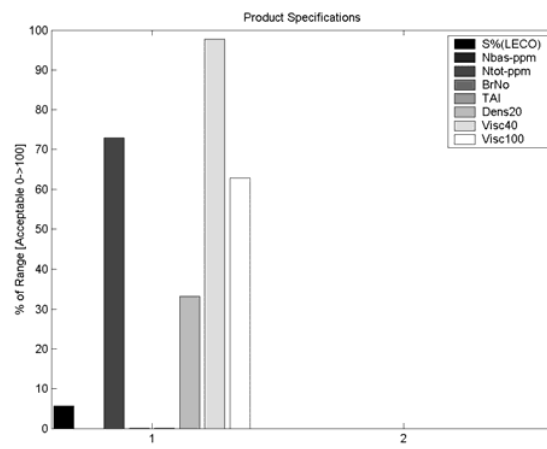
(f)

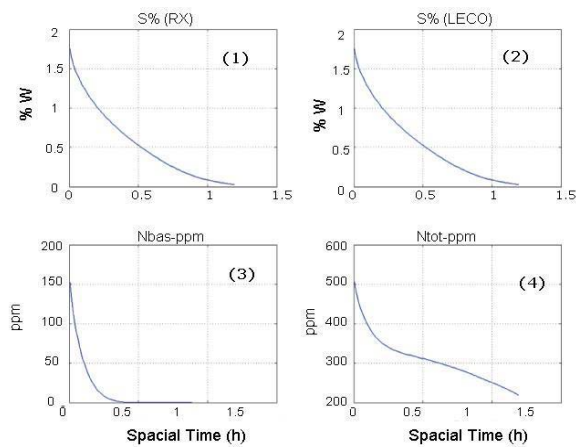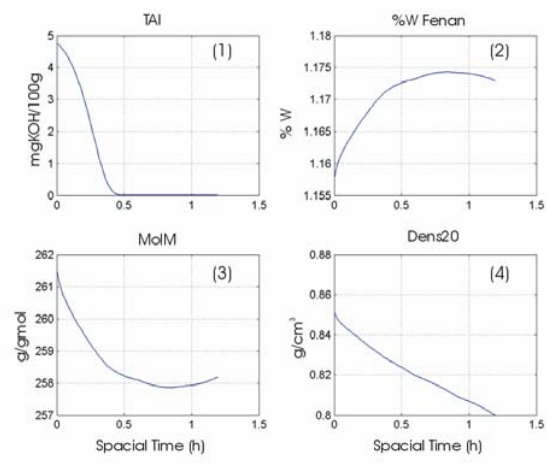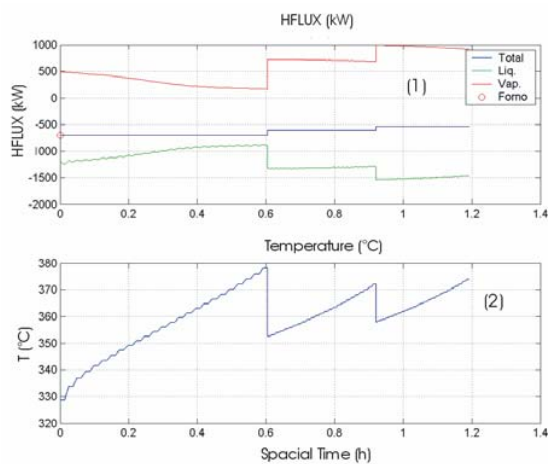(g)   (h)

Figure 2: HDT Optimization Results for Lube Oil (a): Objective function – Annual profit; (b): Optimization of design variables; (c): Product specification vs iteration; (d): Process ISBL vs iteration; (e): Feed specification; (f): Product specification; (g): Process cost path; (h): Process costs.

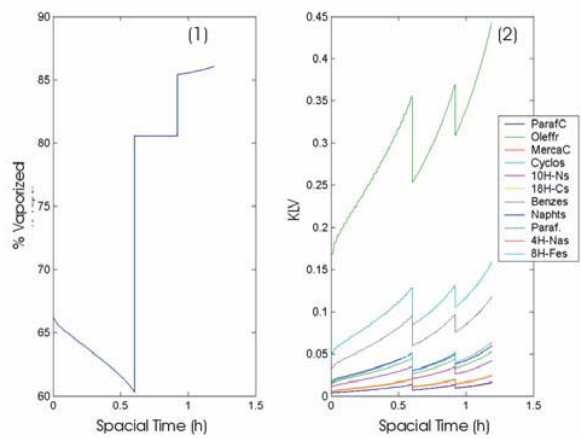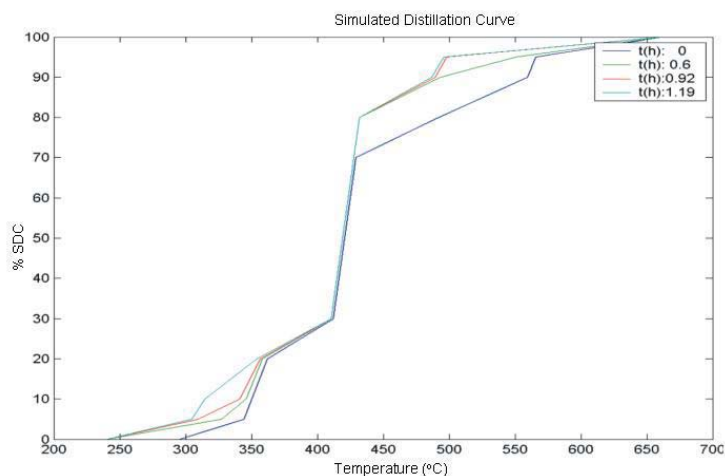(a)   (b)

(c)   (d)

(e)

Figure 3: Profiles for the Reactor (After HDT-LUB Optimum Search): (a) 1: %S (RX); 2: %S (LECO); 3: Basic N; 4: Total N; (b) 1: Br N., 2: Mol. Mass, 3: Density (20ºC), 4: % Fenantrenes; (c) 1: Total Enthalpy and Phases (kW); 2: Temperature (C); (d) 1: % Vaporized (H_2+Oil); 2: LVE Factors; (e) Simulated Distillation Curve for the Reactor.

CONCLUSIONS

A methodology for the lube base oil HDT modeling and optimization process, based on the following: (i) compositional feed modeling; (ii) a preliminary kinetic survey of the extensive reaction network; and (iii) a set of quality aims that must be met. It was shown that an efficient compositional model, together with a rigorous reactor description and simple models for peripheral equipment, is a practical tool for project analysis near optimum conditions.

ACKNOWLEDGMENTS

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