

Development of Intensified Hybrid Equipment: Reactive Molecular Distiller

Winter A.¹, Batistella C. B.¹, Wolf Maciel M. R.¹, Maciel Filho R.¹ and Medina L.C.²

¹ Separation Process Development Laboratory and Laboratory of Optimization, Design and Advanced Control (LDPS/LOPCA), School of Chemical Engineering, State University of Campinas (UNICAMP), P.O.box: 6066 – Zip Code 13081-970 – Campinas – SP – Brazil, phone: +55 19 37883971, fax: +55 19 37883965, winter@feq.unicamp.br

²CENPES/PDP/TPAP/PETROBRAS, Rio de Janeiro-RJ, Brazil.

Studies indicate the existence of fields with so heavy oils that the simple rise and drainage from the base of the oil well to the surface seems to be impracticable in a first analysis, mainly in oil fields Off-Shore. New alternatives, with the objective of reducing the API degree and the viscosity of these oils, are being developed to enable upgrading of the extra-heavy oil. Processes to transform the oil involve thermal or catalytic cracking which imply in transforming large molecules into smaller ones; or simply physical treatments, as extraction of the heavy fractions of petroleum with supercritical fluid or dilution of the oil with fractions of the proper oil, generating the synthetic oil. In this work, a new equipment was developed: the reactive molecular distiller, in which happens simultaneously the coupling of the molecular distillation (high vacuum) and reactive conversion. It is very robust and can be characterized as a hybrid process and also as an intensified process. This equipment will promote the cracking and the conversion of the heavy fractions in lighter ones, which will be injected in the oil well making possible the withdrawal of the heavy oil from the well. Its most important characteristic is the immediate removal of the reaction products, dislocating the equilibrium in the direction of the desired products. The design, construction and studies of Reactive Molecular Distiller will be detailed in this work, which made possible the idealization of this intensified hybrid equipment.

1. Introduction

The first works of the research group LOPCA/LDPS relative to the development of the molecular distillation process was applied for the processing of vegetable oils (Batistella and Wolf Maciel, 1998; Moraes et al., 2004; Fregolente et al. 2007). Nowadays, studies indicate the efficiency of the molecular distillation for separating petroleum residues (Sbaite et al., 2005; Maciel et al, 2006; Winter et al. 2007).

The molecular distillation or short path distillation is not a conventional process; it represents a type of low pressures vaporization, and correspondingly low temperatures. It is indicated for the separation of homogeneous liquid mixtures that contain thermal cracking substances of high molecular weight and low volatility (Erciyas et al., 1987). Molecular distillation involves, basically, two mechanisms: evaporation and condensation, in which vapor molecules escape from the evaporator in direction to the

condenser, where condensation occurs. It is necessary that the vapor molecules generated find a free path between the evaporator and the condenser, the pressure be low and the condenser be separated from the evaporator by a smaller distance than the mean free path of the evaporating molecules (Batistella and Wolf Maciel, 1998; Batistella et al., 2000; Moraes et al., 2004).

Since there is practically not return of the evaporated molecules to the liquid phase (there not exist vapor-liquid equilibrium), the molecular distillation is considered a process of non equilibrium (Hickman, 1943).

Currently, many companies have adopted process intensification, creating innovative techniques and methods increasing the energy efficiency and the yield of the processes.

The combination of chemical reaction and distillation in a unique process has become popular nowadays due to its potential to improve conventional processes design. This combination is advantageous especially for equilibrium limited reactions because the reaction products are continuously removed from the reaction zone. In reactive distillation process the number of equipment and the energy used are frequently much lower than in a conventional process.

The reactive distillation process offer several advantages. It allows increase the yield due to overcoming the chemical and thermodynamic limitation of equilibrium; the selectivity is increased through suppression of undesired consecutive reactions (Noeres et al., 2003); the products are exposed to the heat only once, reducing opportunity for degradation among other things.

In this context, the concept and the equipment of reactive molecular distillation was developed, in which it simultaneously happens the coupling of molecular distillation (high vacuum) and reactive conversion. The configuration of the equipment of molecular distillation allows to submit the material at adequate temperatures (high vacuum process), to have short residence time (operational), and to have a very intense contact of the sample with the catalytic surface. These factors must provide high evaporation rate and high kinetics of reaction, consequently, elevated distillation/conversion rate allowing high processing rates.

2. Materials and Method

The equipment described below corresponds to the Reactive Molecular Distiller that will be used in upgrading heavy and extra heavy petroleums.

The Reactive Molecular Distiller developed (sponsored by PETROBRAS/FINEP, 2007), presented in Figure 1, is constituted by a system for removal the light compounds (volatile at pressure lesser than 10 mmHg) and by the reactive molecular distillation system. All operational utilities are included, such as the vacuum system, heating/cooling systems, the system of pumps and the supervision and control systems.

The operational capacity of the equipment is of 5 to 40 liters/hour what makes possible its use for developing and optimizing processes, and it operates continuously so that good quantity production (pilot plant) is achieved. The temperature can vary from room to 450^oC and the pressure can reach 10⁻³ mmHg. Operations with pressures larger than 10⁻² mmHg make the process inefficient.



Figure 1: Developed Reactive Molecular Distillation Unit; 1 indicates the reactive molecular distiller - 2 indicates the system for removal the light compounds

A test was accomplished before the construction of this reactive molecular distiller in order to evaluate this new concept. The initial experiment was carried out in a centrifugal molecular distiller constructed by the research group (sponsored by FAPESP, Batistella and Wolf Maciel, 1996, 2001) and it was adapted to allow the occurrence of simultaneous chemical reaction and molecular distillation. The results are shown following and they were the basis for building up the new equipment.

3. Results and Discussion

3.1 The previous test

The previous experiment to evaluate the reactive molecular distillation was carried out in a centrifugal molecular distiller that was adapted for the reaction conditions. In the previous experiment, a heavy lubricant oil was submitted to the reactive molecular distillation process. It was added 5% of catalyzer to the lubricant and this mixture was placed in the centrifugal molecular distiller (homogeneous catalysis). The reaction/separation occurred at 350°C and 10^{-1} mmHg. The feed sample and the products obtained in the process were analyzed through gas chromatography with flame ionization detector (CG/FID). The chromatogram of feed sample presents compounds of high molecular weight.

The chromatogram of the distillate sample shows the formation of lighter compounds than those found in the feed sample. This occurred because the heavy compounds were transformed (cracked) in lighter compounds. These results demonstrated that the

reactive molecular distillation method is efficient for cracking and for separating the compounds simultaneously.

Based on these preliminary results and on the difficulties encountered in the experiments, and also by the interest and sponsorship of Brazilian Oil Company (PETROBRAS/FINEP, 2007), a molecular distiller was designed and built up and it is presented in this work. This distiller can be used for homogeneous and heterogeneous catalyses.

3.2 The equipment design and construction

After the conceptual idea and the previous experiment, the new equipment was idealized. The equipment is divided in two systems: the reactive molecular distillation system and the system to removal the light compounds.

3.2.1 System for removal the light compounds

The removal of the volatile compounds is necessary for the effective treatment of the material in the reactive molecular distiller. The presence of volatile compounds influences on the distillation process, damaging the required vacuum level. In this system, it is generated a thin film for increasing the liquid surface area, facilitating the light compound evaporation in a previously defined temperature.

For the efficient removal of the volatile compounds, four variables must be studied: the temperature, the pressure, the residence time of the material and the evaporation surface area of the liquid film. The temperature must be inversely proportional to the residence time of the material being processed. However, it can submit the material to thermal risks. A thermal risk evaluation must be always conducted before establish the system temperature.

The system for removal the light compounds is formed by four subsystems:

- a) Liquid film generation through rotating distributor.
- b) Evaporator surface with heating through electricity.
- c) Thermal control.
- d) System of vacuum generation with trap protection.

This system was designed in a different structure of the molecular reactive distiller for facilitating the operations and experiments in study.

3.2.2 The reactive molecular distiller

The reactive molecular distiller is formed by the evaporator/reactor (heated conical rotor), condenser, vacuum generation system, utilities, pumps system, support and activation systems, control and check of the properties and process (temperature, flow, rotation, etc).

For the equipment design, it was initially defined the diameter measurement of evaporator/reaction surface. This measurement was defined as 400 mm of diameter, which provides feed flow rates of up to 40,0 L/h.

Soon after, it was defined the best middle angle of the rotor. This angle should permit good scattering of the liquid on the rotor surface and also make possible the feed at the central point of the evaporator.

Also, the rotor rotation speed was defined, according to scale-up studies shown in Batistella (2001). The design of the equipment enables the speed adjustment according to the sample. For a very viscous liquid, or thermally sensitive, it is interesting to increase the rotation speed. For a difficult separation product, or of low kinetic rate, the rotation speed can be decreased.

The new equipment concept makes possible the homogeneous or the heterogeneous reaction. The homogeneous catalysis occurs when the catalyzer and the sample are mixed before feed it at distiller. The heterogeneous catalysis will be possible through

the use of catalyzer on evaporator/reaction surface (conical rotor). The conical profile of the distiller provides the intense transfers of heat, mass and momentum, promoting high contact of the liquid with the catalyzer, allowing high kinetic rates, intensifying, so, the process.

The catalyzer installation, in the heterogeneous catalysis, have to be made of homogeneous way on the evaporator surface according to a fine and continuous film avoiding formation of preferential ways. This is possible due to the existence of a frontal opening in the reactive molecular distiller which allows the access to the evaporator surface. The catalyzer adhesion to the evaporator surface can be done through adherent material, since the material allows heating in the order of 300°C. Also, it must present facility to be removed at the catalyzer substitution time.

4. Conclusions

The presented studies in this work show, based on a preliminary idea of reaction/separation scheme from our research group (Batistella et al., 2006), the idealization and the construction of an unpublished reactive molecular distiller.

The new equipment will promote the cracking and the conversion of the heavy fractions in lighter ones. The light components will be injected in the oil well making possible the withdrawal of the heavy oil from the well (upgrade of petroleum).

The reactive molecular distiller constructed owns several facilities: controlled feed flow rate, efficient system for removal the light components, heating lines with high control, evaporator heating system with efficient measurement and control, condenser cooling system with controlled temperature, adjustable evaporator rotation according with the process, high-vacuum system, among others facilities.

The new technology of reactive molecular distillation can be characterized as a hybrid and an intensified process. The most important characteristic is the immediate removal of the reaction products, dislocating the equilibrium in the direction of the desired products.

Nowadays, the equipment is in the automation stage of development and will be able to carry out the experiments of upgrading heavy and extra heavy petroleum.

5. Acknowledgements

The authors are grateful to FAPESP (process number 06/07228-3), FINEP, PETROBRAS and CNPq for the financial support.

References

- Batistella, C. B., Wolf Maciel, M. R., 1996, Purification of fine chemical products through Molecular Distillation, FAPESP Project, Process number 96/0327-2.
- Batistella, C. B. E Wolf Maciel, M. R., 1998, Recovery of Carotenoids from Palm Oil by Molecular Distillation, *Comput. Chem. Eng.*, 22, S53-S60.
- Batistella C.B., Maciel, M.R.W., Maciel Filho, R., 2000, Rigorous Modeling and Simulation of molecular distillations: development of a simulator under conditions non ideality of the vapor phase, *Computers & Chemical Engineering* 24, S1309-S1315.
- Batistella, C. B., Wolf Maciel, M. R., 2001, Development of a Prototype of Centrifugal Molecular Distiller of High Performance, FAPESP Project, Process number 01/10092-2.

- Batistella, C.B., 2001. Design of molecular distillers: from conception of the process to the equipment detail in laboratory, pilot and industrial levels. PhD FAPESP Project, Process number 99/03550-2.
- Batistella, C.B.B., Wolf Maciel, M.R., Maciel Filho, R., 2006, Conceptual and preliminary studies of reactive molecular distillation, Internal Report, LOPCA/LDPS/UNICAMP).
- Erciyas, A.T., Ishikawa, H., Inuzuka, M., Hiraoka, S., Mori, H. E Yamada, I., 1987, Vaporization of Binary Liquid Mixtures from Surface at Reduced Pressure, I.Chem.E. Symposium Series 1, A359-A371.
- Fregolente, L. V. , Fregolente, P. B. L. , Chicuta, A. M. , Batistella, C. B. , Maciel, Filho R. , Wolf-Maciel, M. R., 2007, Effect of Operating Conditions on the Concentration of Monoglycerides Using Molecular Distillation, Chemical Engineering Research & Design 85, 11, 1524-1528.
- Hickman, K. C. D., 1943, High-Vacuum Short-Path Distillation - A Review, Chem. Rev. 34, 51-106.
- Maciel R, Batistella CB, Sbaite P, Winter A, Vasconcelos CJG, Maciel MRW, Gomes A, Medina L, Kunert R., 2006, Evaluation of atmospheric and vacuum residues using molecular distillation and optimization, Petroleum Science And Technology 24, 275-283.
- Moraes, E. B., Batistella, C. B., Torres Alvarez, M. E., Maciel Filho, R., Wolf Maciel, M. R., 2004, Evaluation of Tocopherol Recovery Through Simulation of Molecular Distillation Process, Applied Biochemistry and Biotechnology 113-116, 689-711.
- Noeres, C., Kenig, E. Y., Górak, A., 2003, Modelling of Reactive Separation Processes: Reactive Absorption and Reactive Distillation, Chem. Eng. and Process 42, 157-178.
- PETROBRAS/FINEP, 2007, Development of alternative technology: reactive molecular distillation to transform (upgrading) the extra-heavy oil aiming to improve its draining
- Sbaite, P., Batistella, C.B., Winter, A., Wolf Maciel, M.R., Maciel Filho, R., Gomes, A., Medina, L., Kunert, R., Pontes Bittencourt C., Mathias Leite L.F., 2005, Characterization Of Residue Stream Obtained Through Molecular Distillation Of Heavy Oil Petroleum, The Seventh Italian Conference On Chemical And Process Engineering (Icheap7), Giardini Di Naxos, Taormina, Italy
- Winter A., Batistella C. B., Wolf Maciel M. R., Maciel Filho R., Lopes, M. S., Medina L. C., 2007, A True Boiling Point Curve Through Molecular Distillation Using Framol Correlation, The eight International Conference On Chemical And Process Engineering (Icheap 8), Gulf of Naples.