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Supercritical process technology related to energy and future directions – An introduction

Gerd Brunner*

Hamburg University of Technology, Eissendorfer Strasse 38, D-21073 Hamburg, Germany

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ABSTRACT

Process technology comprises the application of fundamentals to processes, as for example phase equilibria and reaction kinetics, the verification of process steps, as for example in specific reactors, and the design of process sequences to produce a product (energy) from raw materials. For the special field of supercritical fluids related to energy processes it includes single process steps as well as process step sequences and whole processes. Also, process technology is not restricted to any specific application. It includes processing of renewable (bio-based) materials, fossil materials, and processes to access these materials. In general, process technology related to the application of supercritical fluids is based on the exploitation of the specific properties of supercritical fluids. This includes the varying properties of supercritical fluids and the interactions of supercritical fluids with the processes materials, such as a drastically reduced viscosity. Supercritical fluids guarantee an enclosed processing with emanations that can be adjusted. Supercritical fluids have been used in quite a number of processes and process steps related to production of energy, mostly in laboratory and demonstration scale. Among these processes are: the ROSE process, coal liquefaction and gasification, the production of oil from oil shales, and of oil from oil sands. Supercritical fluids have been proposed (and partially are used) for: enhanced oil recovery, emulsion splitting (oil–water), enhanced gas recovery, bitumen separation, recovery of hydrocarbons from particles (remediation of soil), de-asphalting, removal of fine particles, and others. Supercritical fluids are proposed for deep drilling (spallation drilling), and for the production of energy from hydrothermal flames. Process technology using supercritical fluids has to provide the equipment for the processes. Keys to future success will be: simple design, simple operation, high efficiency (higher than burning the feed), and a thorough training of the community in the specific abilities of supercritical fluids.

1. Introduction

The essential topics of interest in our context are “supercritical fluids” and “energy”. Chemical compounds are “supercritical” at temperatures and pressures above the critical temperature and the critical pressure. In this supercritical state, compounds are compressible and their properties change with the pressure applied and enable the tuning of the properties of the process compound without changing the compound itself. The variation of the properties is dramatic in the region close to the critical point of the compound, but still substantial in the region near to the critical point. In combination with supercritical fluids, the properties of materials are physically modified and in many cases enable processing of these materials. Furthermore, chemical reactions in and with supercritical fluids can lead to improved or even unique products. The products can be easily recovered due to the loss of solvent power of depressurized supercritical fluids.

“Energy” in context of this contribution refers to different process applications that can be carried out with supercritical fluids, such as energy transfer, energy transformation, processing of materials useful for producing energy or for recovery of such materials. Energy aspects in general are well known and are intensively discussed. Nevertheless, practical solutions to provide reasonable access to energy are few and are under permanent discussion. Solutions are greatly influenced by non-scientific, non-technical, and political arguments. The combination of supercritical fluids and energy is discussed in the following, considering some process aspects.

2. Introductory example: the ROSE-process

The ROSE process, or “Residual Oil Supercritical Extraction”, is chosen as an example for the application of supercritical fluids related to energy-relevant processes. The ROSE process developed

* Tel.: +49 407909393.
E-mail address: brunner@tuhh.de

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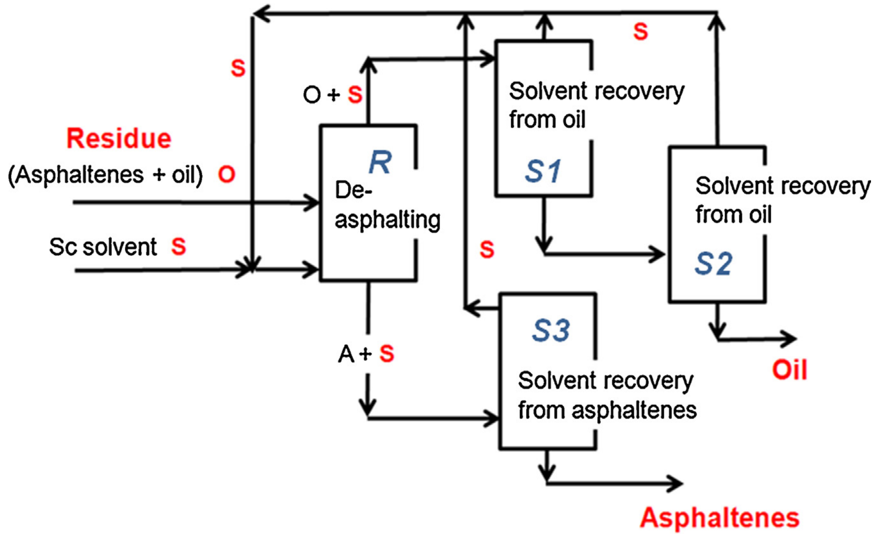

Fig. 1. Simplified flow diagram of the ROSE process. A light paraffinic solvent extracts deasphalted oil from a feedstock rich in asphaltenes. *R* – reactor, *S1* – separator 1, *S2* – separator 2, *S3* – separator 3 (see text).
Modified from Ref. [2].

in the 1950s, abandoned due to the low cost of petroleum during the 1960s, gained life in the 1970s in the so-called first energy crisis. The process separates asphaltenes from mineral oil by using light paraffinic hydrocarbon components, such as pentane [1,2]. A flow scheme of the process is shown in Fig. 1.

The feed of the process is a residue stream, consisting of asphaltenes (A) and oil (O). It is introduced in the reactor (R) and mixed with the supercritical solvent (sc solvent). The sc solvent dissolves the oil and the resulting mixture is transported to a first separator (S1) where the solvent is partially separated from the oil by changing the density of the sc solvent. The density change can be achieved either by pressure reduction or by temperature enhancement. The solvent is added to the recycle solvent stream, while the bottom oil product, still containing solvent, is fed to a second separator (S2), wherein the residual solvent is recovered by reducing the density. Solvent evaporates and the amount of solvent dissolved in the oil is considerably reduced. The residual oil is delivered as the de-asphalted product and the evaporated solvent is recycled. The residue from the reactor (R), consisting of asphaltenes with dissolved solvent, is sent to a solvent recovery unit (S3), where the solvent is separated from the asphaltenes, again by lowering the pressure and such reducing the amount of dissolved solvent in the asphaltene-product.

3. General aspects of application of supercritical fluids to energy related processes

Principles of supercritical fluid processes applied to energy related processes are comparable:

- The supercritical solvent dissolves components of a mixture and forms a separate gaseous phase.
- This phase, formed by the application of the supercritical fluid, is separated from the original mixture, in which part of the supercritical solvent is dissolved, forming the second (liquid) phase.
- From both phases the supercritical solvent is recovered by changing the density.
- The supercritical solvent is then recycled.

4. General areas and aspects of application of supercritical fluids

For what purposes can in general supercritical fluids be used for energy applications? Basically, the ROSE process includes all the process steps that are applied with supercritical fluids, with one exception:

- Direct application of supercritical fluids for heat (energy) transport.

Most of the applications of supercritical fluids in connection with energy can be summarized as follows:

- Application of supercritical fluids to exploit their solvent power and make effective use of the variation of the solvent power.
- Application of supercritical fluids for carrying out reactions, in particular with compounds of renewable resources.
- Applications of supercritical fluids to fossil fuels, with respect to their recovery, conversion, and formulation.
- Application of supercritical fluids for direct recovery of energy, for example with hydrothermal flames.
- Application for saving energy, for example due to solvent recycling.

Supercritical fluids are a process tool. Therefore, the task is to consider processes that use supercritical fluids, rather than to design processes for supercritical fluids. In a similar way, processes use phase changes from liquid to gas, as for example in distillation. Process technology comprises the application of fundamentals to processes, as for example phase equilibria and reaction kinetics, and their verification in process steps in specific reactors, and the design of process sequences to produce a product (including energy!) from raw materials.

The application of supercritical fluids to energy-related processes also includes single process steps as well as process step sequences and whole processes. These energy-related processes are not restricted to a specific application, but can be applied to processing of renewable (bio-based) materials, fossil materials, and any process to access these materials.