THERMODYNAMICS FOR THE OIL INDUSTRY. UPSTREAM (CRUDE OIL EXTRACTION & FLOW ASSURANCE). DOWNSTREAM (NEW GENERATION OF BIOFUELS FOR THE AUTOMOTIVE INDUSTRY)

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Extracting crude oil from porous rocks in deep inshore and offshore deposits is still of paramount importance for providing petroleum despite the progresses made for replacing fossil oil exploitation by otherwise developed technologies (nuclear, solar, wind, biofuels). In this context oil extraction and intrusion/extrusion of liquids in/from porous media present similar thermodynamic aspects, including in the car industry designing engine injectors to be used with newly developed biofuels to be injected under high pressure through extremely narrow (even nano) holes. Experimental contributions can provide unique high quality data to make decisive technological progresses in both the oil industry and the automotive industry.

Calorimetric measurements under *P*, *V*, or *T* - scans over extended temperature and pressure ranges open new perspectives. A major step was the development of a new technique, *Scanning Transitiometry* (see website www.transitiometry.com) which is remarkably suited to determine thermodynamic and thermophysical properties of matter, gases, and liquids, including supercritical fluids, and polymers under extreme conditions of temperature and pressure, namely: 173 K <*T*< 673K and 0.1 MPa <*P*<400 MPa. The original contribution of *Scanning Transitiometry* is illustrative of the power of this technique.

In the oil industry two important areas are concerned: heavy oil and light condensed gas mixtures. Oil fields and deposits which are currently exploited and new ones to be exploited represent a prospect of huge reserves of oil. Nevertheless, in most of these reserves the presence of asphaltenes and waxes and their aggregation and precipitation pose technological problems for the prevention of the plugging of installations and of transport pipes with all consequent economic and environmental costs. To prevent these phenomena a good knowledge of the thermodynamic behavior of phase equilibria - *i.e.* the asphaltene precipitation envelope (APE), as well as the bubble pressure (BP) of the crude oil - in such complex systems is essential. To this end, one must be able to reproduce at the laboratory level the real in-well conditions in terms of temperature and pressure. Experimentally the challenge is then to implement the operational techniques to work on live oils under real in-well conditions.

The major, pivotal, role also played by *Scanning Transitiometry* is stressed by its capacity to in-depth provide the whole set of thermomechanical properties of homogeneous fluids. Naturally, these results have led to characterizing automotive fuels, particularly the new generation of (synthetic) biofuels, for which investigations were carried in a partnership with leading representatives of the car and oil industries. The reference fuel, Shell Normafluid, was used to show the type and quality of the data generated in the temperature range from 253 to 423 K, up to 200 MPa. The present contribution reports the determination of isobaric thermal expansivities α_P in the same range of temperatures and pressures and how obtained data permit to derive other thermophysical properties such as heat capacities C_P, and isothermal compressibilities κ_T over extended temperature and pressure ranges for a series of biofuels. Other properties, highly important for the automotive industry as well as for some crude oils (light condensed gas mixtures), like bulk modulus (or adiabatic compressibilities) and Joule-Thomson coefficients are generated there from.

References

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