A Novel Petrochemistry Solution: SARA Fractionation of Crude Oil Using an Adaptable Gilson MPLC System

Authored By:
Freddy Moy and Fabrice Mangani – Gilson BV France & Toni R. Hofhine – Gilson, Inc.

Technical Note 0312

Overview

Petroleum consists of a complex hydrocarbon mixture, result of a slow process of nature (thousands of years) issued from sediment deposits which contained microorganisms, animals and plants. Due to the successive sedimentary rock layers accumulation, under Heat and Pressure, organic matter has been transformed into Kerogen and finally into Oil and Gas.

Crude oil is mainly composed by hydrocarbons and derived organic sulfur, nitrogen, oxygen and organometallic, composition which depends directly on location, age and depth. The hydrocarbons in oil can be classified into four main classes based on polarity and solubility (see Figure 1):

- **S**aturated (alkanes and cycloparafinns)
- **A**romatics (hydrocarbons, mono, di and polyaromatic)
- **R**esins (polar molecules with heteroatoms N,O,S)
- **A**sphaltenes (similar to the resins with higher molecular weight and polyaromatic core)

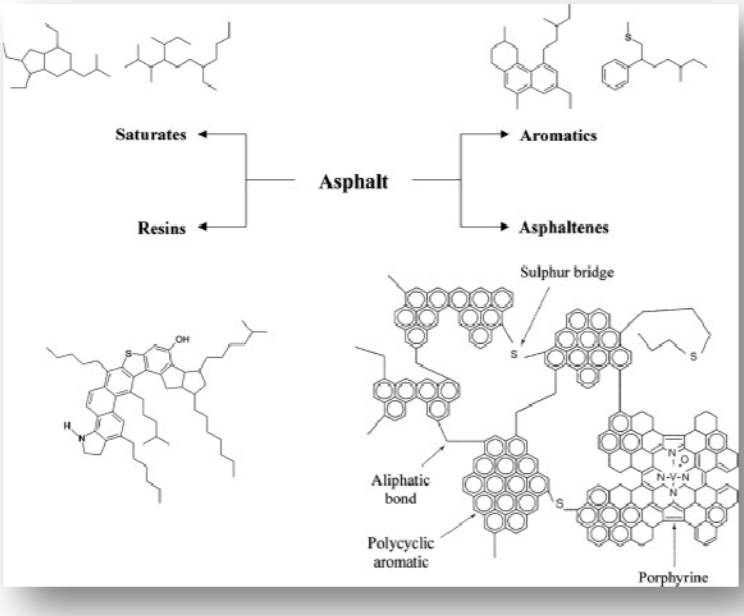

Figure 1:

Structures of four main hydrocarbon classes
(image from ScienceDirect.com)

Gilson, Inc. World Headquarters
Middleton, WI 53562 USA
Telephone: 800-445-7661

Oil composition determination constitutes a key point from geochemists to the refiners, from the rock degradation degree to the amount of heavy organic dissolved and suspended solids precipitation. Results from SARA analysis are used as a quality indicator of oils and bitumens. Analysis results of the SARA fraction proportions are also used to calculate the asphaltene stability within the oil.

Final SARA analysis is not possible without sample preparation prior to a variety of published analysis methods, such as GC, GC/MS and Isotopes analysis. Gilson has developed a novel petrochemistry solution to enable SARA fractionation (i.e. sample preparation) using an adaptable Gilson MPLC (Medium Pressure Liquid Chromatography) System.

Materials & Methods

The Gilson MPLC System (see Figure 2) is dedicated to the separation and sample preparation of deasphatened solution (maltene) obtained after nPentane addition in Crude oil and asphaltene fraction precipitation. Maltene extract has separated with our MPLC (Medium Pressure Liquid Chromatography) system into 3 fractions: Saturates, Aromatics, Resins. Up to 100 mg of extract can be injected and separated to allow for both the traditional gravimetric quantification of each fraction and also additional final analysis (as described above) separate from the MPLC system.

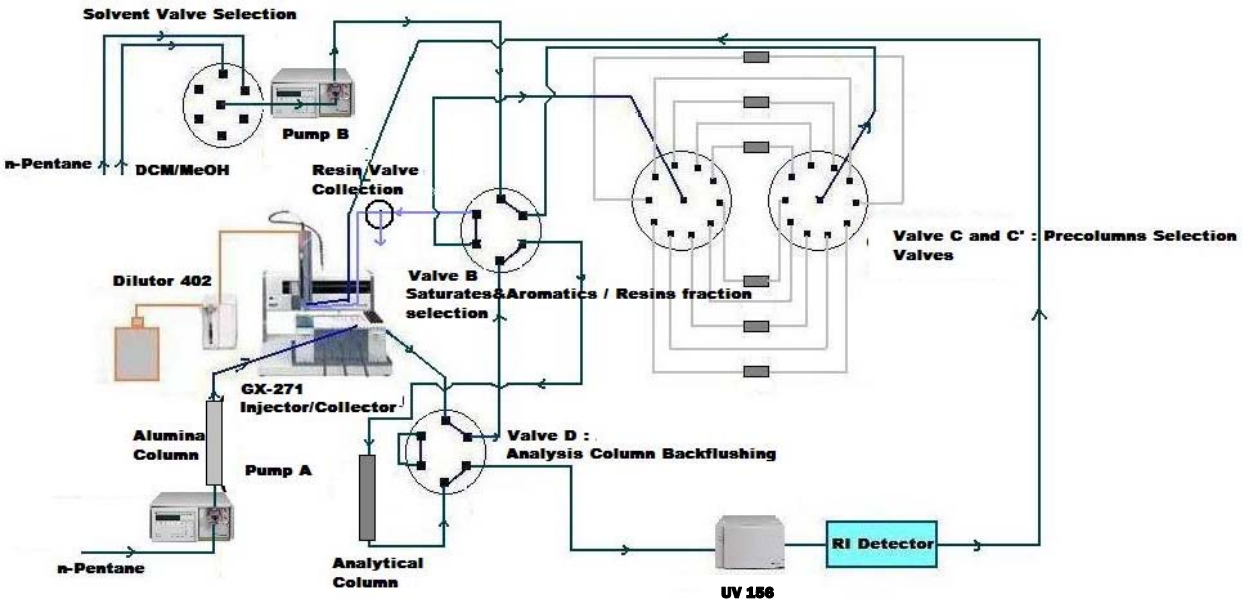

Figure 2: Gilson MPLC System for SARA Fractionation of Crude Oil

The Gilson MPLC System Description for SARA Fractionation in Crude Oil:

- GX -271 Liquid Handler with Dilutor 402:
    - aspirates and injects samples into an injection loop via two independent collection valves
    - all fractions are collected into evaporation flasks through the fraction valve on the GX-271 Liquid Handler
- Two 307 Single Piston Isocratic Mobile Phase Pumps (Pumps A and B) are used to generate the process range mobile phase flow rates (8-10 ml/min):
    - flows through silica gel pre-columns and an activated silica analytical column are implemented
    - prevent damage of the analytical column during the SAR separation and maintain good separation reproducibility between sample injections, the Gilson MPLC System avoids any presence of polar solvent through the analytical column
        - pump A is dedicated to the conditioning and fraction collection step of Saturates and Aromatics
        - pump B allows the fraction collection of resins through the final back-flushing of pre-columns
        - for additional security, the mobile phase from Pump A can be passed through an Alumina Column
- Five VALVEMATE® II column switching valves provide full automation:
    - Valve A: selects up to 6 different solvents for the rinsing steps and for the resins elution steps.
    - Valve B : isolates the analytical column during resins elution steps
    - Valve C & C': provide automatic pre-column selection according to current sample injected, and up to 6 samples can be prepared during one application sequence
    - Valve D : provides analytical column back-flushing for aromatics fraction collection
- Refractive Index Detector Gilson 156 UV detector:
    - validates the SAR separation and fraction collection timing

The Typical Gilson MPLC Sample Sequence (see Figure 3):

1. Pre-columns (silica gel) and analytical column (activated silica) are conditioned with Pump A.
2. After injection (typically 1ml of sample), the sample passes through the pre-column and analytical column in a 'serial' configuration using Pump A The saturates are collected.
3. After Valve D switching and the analytical column back-flushing, aromatics are automatically collected into another evaporation flask.
4. After Pump A stops and Valve B switching isolates the analytical column, the resins fraction is collected from the pre column in 'back-flush' mode with Pump B flow rate and resin elution solvent selection (Valve A) into another evaporation flask via a 2nd collection valve.
5. The Valve C and C' are incremented by one position and placed in 'by-pass' position. After Rinsing solvent selection on Valve A, the system is rinsing before the next sample injection.

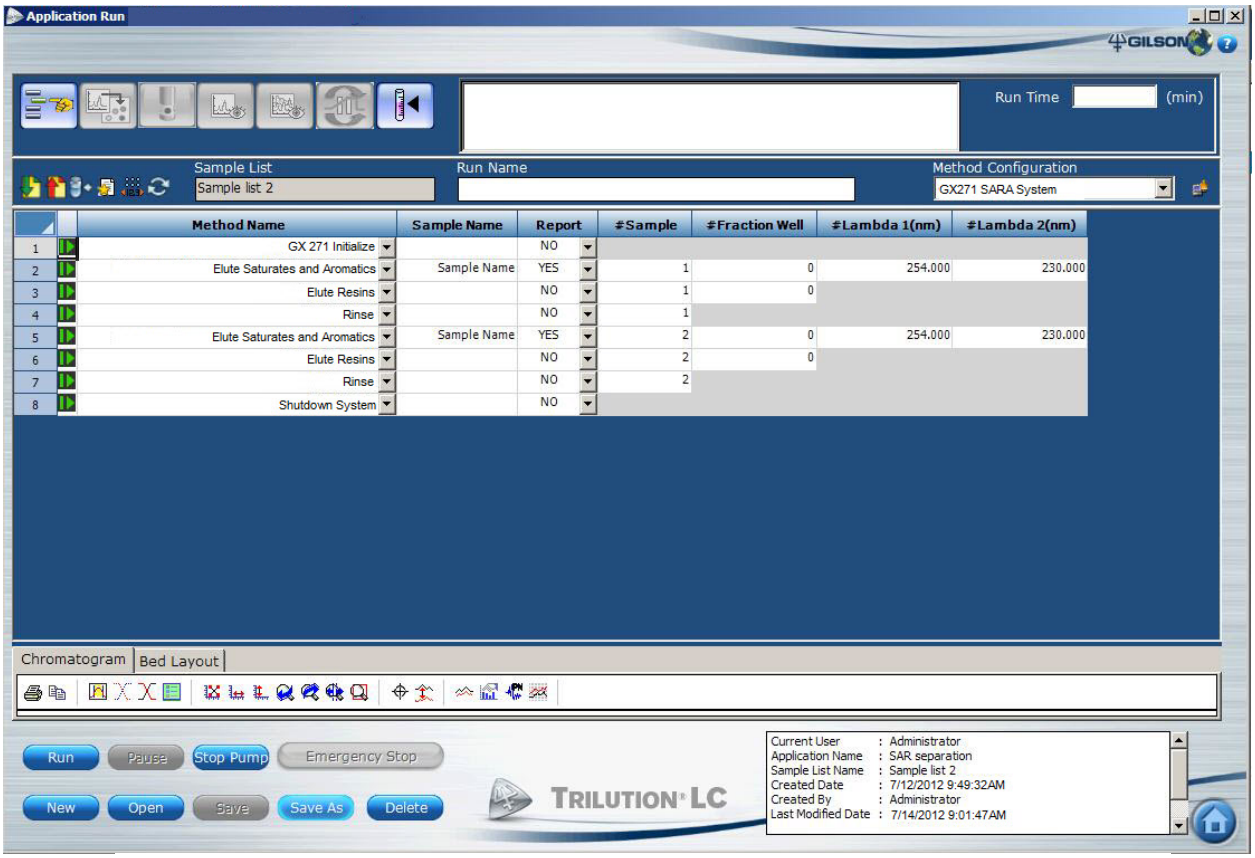

Figure 3: Gilson TRILUTION LC v2.1 Sample Sequence (Operations List shown)

Technical Summary

SARA fractionation of crude oil using the Gilson MPLC System produces highly desirable chromatography and reproducible separations. RSD retention times are approximately 2%. Excellent recoveries of each fraction of the SAR separation were >98%, with a CV around 0.6% (see Figure 4).

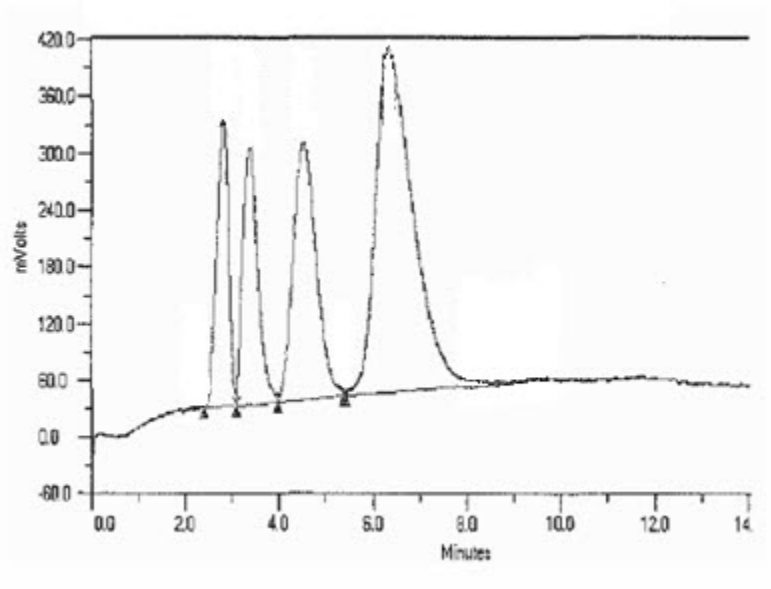

Figure 4: Gilson MPLC System Results - Test Mixture Injection
(from left to right: decane, decene-1, deca-1,9 diene, n-butylbenzene)

Multiple columns allow for fraction collection of SAR using the adaptable MPLC platform. Up to 100 mg of deasphatened sample extract can be injected and separated using the Gilson MPLC System. Traditional gravimetric quantification of each fraction can be performed, as well as final additional analysis as a result of the sample preparation.

Questions? Please Contact Us

If you have application questions related to this technical note or if you are interested in further information on the Gilson system configurations discussed, please feel free to contact us:

Gilson Applications (within the Gilson Knowledge Center Department)
Email: applications@gilson.com
Phone: 1-800-445-7661 OR 1-608-836-1551