



## Development of oxazolidines derived from polyisobutylene succinimides as multifunctional stabilizers of asphaltenes in oil industry

Violeta Y. Mena-Cervantes<sup>a,\*</sup>, Raúl Hernández-Altamirano<sup>a</sup>, Eduardo Buenrostro-González<sup>a</sup>, Hiram I. Beltrán<sup>b</sup>, Luis S. Zamudio-Rivera<sup>a,\*</sup>

<sup>a</sup>Programa de Ingeniería Molecular, Grupo de Química Aplicada a la Industria Petrolera, Instituto Mexicano del Petróleo, eje Central Lázaro Cárdenas No. 152 col. San Bartolo Atepehuacan, México, DF 07730, Mexico

<sup>b</sup>Departamento de Ciencias Naturales, DCNI, Universidad Autónoma Metropolitana (UAM), Unidad Cuajimalpa, Pedro Antonio de los Santos 84, San Miguel Chapultepec, DF 11850, Mexico

### HIGHLIGHTS

- ▶ Polyisobutenyl oxazolidines were developed as multifunctional stabilizers of asphaltenes.
- ▶ Structural design of three novel oxazolidine prototypes is discussed.
- ▶ Small structural differences produce important changes in asphaltenes control performance.
- ▶ The best stabilizer was evaluated at industrial scale in an active production well.
- ▶ The injection of novel prototype produced important technical-economic benefits.

### ARTICLE INFO

#### Article history:

Received 30 March 2012  
Received in revised form 16 December 2012  
Accepted 18 December 2012  
Available online 11 January 2013

#### Keywords:

Asphaltene inhibition  
Fouling  
Heavy organics  
Petroleum  
Polyisobutylene succinimide

### ABSTRACT

The aim of the research presented herein was to develop novel multifunctional stabilizers of asphaltenes (**Asph**) for the control of fouling in different stages of petroleum industry. Novel stabilizers were obtained from the reaction between polyisobutenyl succinic anhydride (**PIBSA**), 2-(2-aminoethylamino)ethanol (**AEAE**) and an R-substituted aldehyde, resulting in three 2-R-(polyisobutylenesuccinimidyl)oxazolidines as prototypes of multifunctional **Asph** stabilizers, where R is –H (**P1**), –C<sub>5</sub>H<sub>11</sub> (**P2**) or –*ortho*(OH)C<sub>6</sub>H<sub>4</sub> (**P3**). Compounds **P1–3** were characterized by FTIR, <sup>1</sup>H, <sup>13</sup>C and 2D NMR spectroscopies, and assessed in four different types of evaluations: (i) **Asph** dispersion by UV–vis, (ii) displacement of **Asph** onset precipitation, at ambient conditions, (iii) inhibition of electric field induced deposition of **Asph**, and (iv) displacement of **Asph** onset precipitation, at reservoir conditions. All the latter individual efficiencies were included in a multifunctional development factor (MDF) resulted in 0.626 for **P1**, 0.326 for **P2**, and 0.679 for **P3**, where the higher value corresponded to the highest efficiency. For comparison purposes, two commercial stabilizers of **Asph** were also evaluated, resulting in MDF of 0.012 and 0.162, being **P1–3** clearly better multifunctional chemicals. Best novel prototype was selected for industrial evaluation by taking into account technical and economic criteria, thus **P1** compound was chosen as active component of **DAIM** chemical and was successfully assessed at industrial scale in a production well of Petróleos Mexicanos (PEMEX) to control **Asph** fouling. The continuous injection of **DAIM** produced important benefits to the oil well productivity, such as the decrease of the frequency of cleaning operations from 11 to 4 in a one-year evaluation period and the reduction of production rate decay from –1.48 to –0.032 m<sup>3</sup>/day, ca. 46 times less in comparison when the well was operated without **Asph** stabilizer.

© 2013 Elsevier Ltd. All rights reserved.

### 1. Introduction

Lack of asphaltene stability within crude oil can occur at any stage of petroleum production or processing, from petroleum reservoir to refinery facilities, precipitation and deposition of this heavy

organic compounds cause important economic losses to the industry every year [1–4]. Normal management of crude oil wells with problematic asphaltenes (**Asph**) fractions can cause fouling in initial stages of the exploitation, therefore under severe operation conditions the closing of the well follows. Important enhancements in the depletion of wells as well as inhibition of fouling in industrial facilities have been encountered with the continuous low dosage of multifunctional chemicals, showing advantages in terms of bene-

\* Corresponding authors. Tel.: +52 5591757059.

E-mail address: [nymena@gmail.com](mailto:nymena@gmail.com) (V.Y. Mena-Cervantes).

fit – cost ratio. Successful chemical products have exhibited control over the problematic **Asph** fraction in two important ways:

- (1) When the chemical is capable to displace the onset of **Asph** precipitation under reservoir conditions, implying high pressure and high temperature ranges [5,9–11], it is classified as inhibiting effect (**IE**). Traditionally polymeric molecules are employed as inhibitors of **Asph** [5–8].
- (2) When the chemical is able to stabilize aggregates of **Asph** as their dispersions under ambient conditions, implying atmospheric pressure and moderate temperature ranges, it is classified as dispersant effect (**DE**). Traditionally low weight amphiphilic molecules are used as **Asph** dispersants [5,9–11].

Despite their differences, inhibitors and dispersants of **Asph** possess two basic structural features: a polar fragment that provide the interaction towards polar parts of **Asph**, and an apolar fragment that provide as well interaction towards apolar parts of **Asph** and miscibility within hydrocarbon medium.

Several approaches have been conducted in order to investigate the role of the polar (head) and apolar (tail) fragments present in synthetic **Asph** dispersants in order to enhance their performance [6,8,9,12–15]. It has been observed that head group provides the interaction site of surfactant molecule towards **Asph** and that the strength and stability of such interaction is highly dependent on fine donor–acceptor acid–base structural characteristics. Whereas, the hydrophobic tail functionality is responsible to provide a lyophilic steric barrier or enclosure to the ensembles made of surfactant–**Asph** dyads. Although a lot of intends to gather the best head and tail fragments into a multifunctional **Asph** stabilizer have been performed, the results are incipient and no clear tendencies were found in the literature.

Starting from these facts, the investigation presented herein focuses on the development of multifunctional molecules containing proper structural features to stabilize **Asph** in crude oil at different stages of its exploitation and processing.

## 2. Experimental

### 2.1. Reagents and benchmarking of chemical products

Polyisobutenyl succinic anhydride (**PIBSA**) of  $M_n = 1098 \text{ g mol}^{-1}$  was purchased from BASF and further purified through a silica chromatographic column to separate it from the remaining polyisobutylene (**PIB**) present in raw material. Reagent grade 2-(2-aminoethylamino)ethanol (**AEAE**), paraformaldehyde, hexanal and 2-hydroxybenzaldehyde were obtained from Aldrich while *n*-heptane of HPLC grade and silica gel at 40–60 mesh were purchased from J.T. Baker and used without further purification.

Two chemicals were selected for benchmarking and comparison purposes: Dodecylbenzene sulfonic acid (**DBSA**), which has been extensively reported in specialized literature as synthetic **Asph** dispersant [12,16–20], and a commercially available **Asph** stabilizer (**CPA**) based on polyisobutylene.

**DBSA** 90% purity was purchased from Fluka and used without further treatment, while commercial product **CPA** sample was supplied by Petróleos Mexicanos (PEMEX), this sample was treated at reduced pressure to eliminate volatile components in order to leave the active product for tests and comparison.

### 2.2. Crude oil characteristics

The evaluation of the new compounds as inhibitors–dispersants of **Asph** was carried out using a light Mexican crude oil from

southeast fields that has a known tendency for precipitation of **Asph** during production operations, its main physicochemical characteristics are presented in Table 1.

### 2.3. Engineering and preparation of 2-*R*-substituted-(polyisobutylene-succinimidyl) oxazolidines (P1-3)

#### 2.3.1. Design of P1-3 compounds

Modulation of polarity and functional geometry can be controlled in a given molecular structure by the introduction of adequate representative substituents. In first place, highly branched polyisobutenyl moiety was selected as *tail group* in order to provide an enhanced steric barrier. On the other hand, typical polar *head groups* for dispersants are of aromatic nature, meanwhile the polar *head groups* for inhibitors are constituted with polar heteroalkyl substituents. In this line, the employment of a non-aromatic heterocyclic *head group* is aimed to gather both characteristics present in individual inhibitors or dispersants but in this case included in the same molecular structure. Therefore, three structural alternatives were established for *head group* depending on the nature of the substituent directly bonded to a non-aromatic heterocyclic *head group*, in this case chosen as the oxazolidine ring. In the first case, the *R* substituent in position 2 of the oxazolidine was a hydrogen atom, **P1**, representing the simplest option. The second prototype, **P2**, presented an *n*-pentyl substituent also in position 2, which introduced an additional hydrophobic spacing element. And a third prototype was synthesized with *ortho*-hydroxybenzyl substituent, **P3**, as an aromatic polar derivative in order to enhance the interaction with **Asph**.

#### 2.3.2. Preparation of compounds P1-3

The synthetic route of three novel 2-*R*-substituted-(polyisobutenylsuccinimidyl) oxazolidines **P1-3** was carried out in absence of solvent and its summarized in Scheme 1. The general path consists of two stages [21,22]:

- stage (i) solventless addition–condensation coupled reactions between **PIBSA** and **AEAE** resulted in the obtaining of the intermediate product polyisobutenyl *N*-(hydroxy)alkyl succinimide (**PIBSI**), see Scheme 1;
- stage (ii) solventless condensation reaction between **PIBSI** and paraformaldehyde, hexanal or 2-hydroxybenzaldehyde at 140–160 °C, to obtain novel prototypes **P1-3** in yields higher than 95%, all compounds were isolated as viscous and dark yellow liquids.

#### 2.3.3. Spectroscopic characterization of P1-3 compounds

The compounds **P1-3** were spectroscopically characterized by FTIR,  $^1\text{H}$ ,  $^{13}\text{C}$  and 2D NMR techniques. The IR spectra were recorded in the range of 4000–400  $\text{cm}^{-1}$ , on a Bruker Tensor-27 FT-IR spectrometer, using ATR technique. The NMR experiments were performed on a Varian Mercury 200-BB spectrometer. The  $^1\text{H}$

**Table 1**  
Properties of oil W-1.

Density ( $\text{g/cm}^3$ )	0.845
$^\circ\text{API}$	36.7
Acidity (mg KOH/g)	0.1
Solids in suspension by centrifugation (%w)	2.14
Toluene insolubles (%w)	0.03
Wax (%w)	5.75
<i>n</i> -heptane Asphaltenes (%w)	0.56
Saturates	63.66
Aromatics	24.11
Resins	11.68

Download English Version:

<https://daneshyari.com/en/article/6640867>

Download Persian Version:

<https://daneshyari.com/article/6640867>

[Daneshyari.com](https://daneshyari.com)