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# Pilot-scale evaluation of hydrotreating inferior coker gas oil prior to its fluid catalytic cracking

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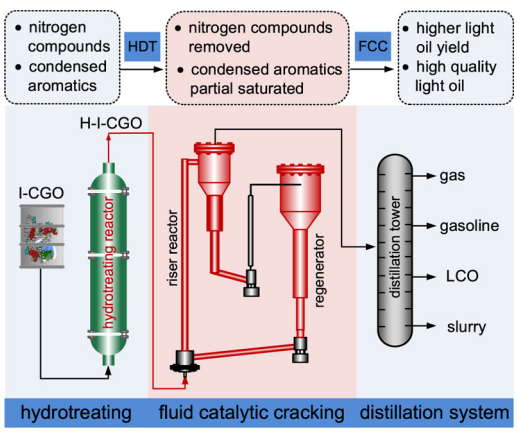
## GRAPHICAL ABSTRACT

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## ABSTRACT

Inferior coker gas oil (I-CGO) is difficult to directly process by fluid catalytic cracking (FCC) or hydrocracking owing to its high content of nitrogen and condensed aromatics. Catalysts in these units deactivate rapidly as a result of major coking and acid site neutralization. In this work, a two-step pilot-scale process consisting of hydrotreating I-CGO followed by FCC processing is designed to effectively convert I-CGO to high-value light fuel product. The results showed that the yield of gasoline increase by 12.88 wt%, whereas the yield of the slurry decrease by 20.55 wt%. Moreover, the quality of the products; including gasoline, light cycle oil (LCO), and slurry improved, significantly. These remarkable results arise from a synergy attributed to the ease of cracking of partially saturated condensed aromatics without major coking as well as reducing the content of basic nitrogen.

*Abbreviations:* CCR, conradson carbon residue; CGO, coker gas oil; FCC, fluid catalytic cracking; FBP, final boiling point; GC–MS, gas chromatography-mass spectroscopy; HDT, hydrotreating; HDS, hydrodesulfurization; HDN, hydrodenitrogenation; I-CGO, inferior coker gas oil; LCO, light cycle oil; LHSV, liquid hourly space velocity; LPG, liquefied petroleum gas; H-I-CGO, hydrotreated inferior coker gas oil; IBP, initial boiling point; PONA, paraffins, olefins, naphthenes, and aromatics; PAH, polyaromatic hydrocarbons; RON, research octane number; SARA, saturates, aromatics, resins, and asphaltenes; VPO, vapor pressure osmometry

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## 1. Introduction

Venezuela's vacuum residue, widely known as Venezuela's inferior heavy oil, is characterized by low hydrogen to carbon atom ratio (H/C = 1.41), high conradson carbon residue (21.15 wt%) and high content of heteroatoms and asphaltenes (12.41 wt%) [1]. Subsequently, delayed coking is the most effective conversion process for Venezuela's inferior heavy oil. Delayed coking is a relatively low capital and operating expense process, since it does not require a catalyst, and is easily adaptable for different feedstocks [2,3]. Coker gas oil (CGO) accounts for 20–30 wt% of the total coking products, which makes it an appreciable stream, especially when heavy crude is fed to a refinery [4]. Despite the extensive cracking, CGO derived from Venezuela's inferior heavy oil, known as inferior CGO (I-CGO), displays worse qualities than a regular CGO, which limits its further processing using FCC. The large volume of this stream, on the other hand, mandates the design of innovative techniques for its processing.

Many researches reported challenges with processing regular CGO using FCC, due to its high content of nitrogen (especially basic nitrogen) and condensed aromatics as well as its hydrogen deficiency [5–7]. Basic nitrogen compounds readily interact with Brønsted acid sites and/or Lewis acid sites, leading to rapid FCC catalyst poisoning [5,8–10]. Catalyst deactivation restricts the conversion of the feedstock and reduces the yield of the valuable liquid products [5,8–10]. Moreover, non-basic nitrogen compounds and condensed aromatics are difficult to crack. Rather, they easily condense to form coke under FCC operating conditions [8], which further deactivates FCC catalyst and complicates CGO processing. Lastly, the adsorption tendency of nitrogen compounds and condensed aromatics is higher than that of the naphthenes and alkanes [11] rendering them the first to occupy the catalyst active sites, which restrains the adsorption and cracking of the naphthenes and the alkanes. Despite these difficulties, feasible approaches had been proposed by many researchers for processing regular CGO by FCC unit. For example, Wang et al. [5] proposed limiting the blend ratio of regular CGO with vacuum gas oil in the FCC feedstock. In addition, having proper catalyst acidity and high accessibility to the active sites under controlled reaction conditions provided a workable solution for FCC processing of CGO [5]. A divisional FCC process for direct catalytic cracking of regular CGO was explored by Li et al. [12]. A separate reaction zone was designed to reduce the content of nitrogen compounds and aromatics, hence attenuate their adverse effect on the FCC catalyst. Fine tuning of the operating conditions for each reaction zone improved the conversion and enhanced the quality of the light oil product. Other innovative FCC processes also reported effective conversion of regular CGO [13–16]. Nevertheless, none of these processes considered I-CGO. As stated earlier, the quality of I-CGO is worse than that of regular CGO, which renders the literature approaches of direct FCC processing of regular CGO inapplicable. Subsequently, pre-treatment of I-CGO prior to FCC processing constitutes an attractive alternative. Four different pre-treatment approaches had been proposed in the literature; namely solid adsorbents [17], neutralization [18], solvent extraction [19–21], and hydrotreating (HDT) [4,22]. Problems associated with the first three methods include low yield, high energy consumption, and serious environmental footprint. HDT, on the other hand, appears viable, especially given its long history of commercial-scale applicability. It should be noted that HDT is currently being applied for the conversion of regular CGO through blending it with other HDT feedstocks [23–26]. Nevertheless, only few studies considered HDT of I-CGO mainly due to the adverse effect of I-CGO on HDT catalyst life, even at low blending ratios [27]. Therefore, the HDT catalyst must be specially designed to adapt to the higher content of basic nitrogen and condensed aromatics.

In this work, a pilot-scale process consisting of successive HDT and FCC processing for the efficient conversion of I-CGO into light fuel oil is evaluated and optimized. HDT reduces the potential of FCC catalyst deactivation via improving the cracking ability of the nitrogen compounds and the condensed aromatics as well as removing the heteroatoms from I-CGO [23,26,28–31]. Nevertheless, the HDT catalyst has to be specially adapted to the nature of the I-CGO feedstock. The extent of I-CGO hydrogenation is controlled to optimize hydrogen consumption [32,33], and the FCC process is optimized to maximize the conversion and the yield of light fuel oil product. In order to provide a thorough understanding of the combined process, the nitrogen contents (including basic nitrogen) and hydrocarbon composition (including paraffins, naphthenes, aromatics, thiophenes, and resins) of I-CGO before and after HDT were analyzed. FCC of I-CGO and H-I-CGO feedstocks were conducted to provide a comparison. The properties of FCC products from the I-CGO and the H-I-CGO feedstocks were also analyzed.

**Table 1**
Properties of I-CGO and some regular CGO's.

| Item | I-CGO | Daqing CGO | Dagang CGO | Liaohe CGO |
|---|---|---|---|---|
| Density (20 °C), kg·m$^{-3}$ | 963.4 | 862.8 | 910.2 | 963.4 |
| CCR, wt% | 0.45 | 0.095 | 0.12 | 0.15 |
| Molecular weight (VPO) | 341 | 283 | 308 | 355 |
| Elemental composition | | | | |
| Carbon, wt% | 85.84 | 85.15 | 85.93 | |
| Hydrogen, wt% | 11.23 | 12.83 | 11.69 | |
| Sulfur, μg·g$^{-1}$ | 27,219 | 2000 | 7800 | |
| Total nitrogen, μg·g$^{-1}$ | 5078 | 3400 | 5400 | 6900 |
| Basic nitrogen, μg·g$^{-1}$ | 1494 | 1100 | 1600 | 2639 |
| H/C atom ratio | 1.57 | 1.81 | 1.63 | 1.52 |
| SARA analysis, wt% | | | | |
| Saturates | 33.40 | 78.80 | 60.84 | 59.34 |
| Aromatics | 58.80 | 12.60 | 30.47 | 27.28 |
| Resins | 7.80 | 8.60 | 8.69 | 12.54 |
| Asphaltenes | 0 | 0 | 0 | 0.84 |

## 2. Experimental section

### 2.1. Feedstock and catalyst

I-CGO feedstock was derived from a delayed coking unit in a Chinese refinery processing vacuum residue from Venezuela's Mery-16 crude oil. The properties of the I-CGO feedstock are listed in Table 1. For comparison, the properties of CGO from Daqing [5,11], Dagang [12] and Liaohe [11] are also presented in Table 1.

A NiMo/$Al_2O_3$ catalyst was employed for HDT I-CGO, the surface area, pore volume, and bulk density was 148 m$^2$·g$^{-1}$, 0.26 cm$^3$·g$^{-1}$, and 1.25 g·cm$^{-3}$, respectively. $MoO_3$ and NiO accounted for 15–30 wt% and 4–10 wt%, respectively, of the catalyst. The FCC catalyst used in this work was a typical commercial equilibrium LVR-60 FCC catalyst, with detailed properties listed in Table 2.

### 2.2. Equipment and procedure

The HDT of I-CGO experiment was performed in a pilot hydrogenation unit, as shown in Fig. 1. This unit includes gas controlling system, oil inlet system, preheating system, reaction zone, and hydrogenated oil-gas separation system. The $H_2$ (99.9995% pure, Beijing Huanyu Jinghui City Gas Technology Co. LTD, China) volumetric flow

**Table 2**
Properties of commercial equilibrium FCC catalyst LVR-60.

| Microactivity index | Filling density, g·ml$^{-1}$ | Settlement density, g·ml$^{-1}$ | Metal content, μg·g$^{-1}$ | | |
|---|---|---|---|---|---|
| | | | Ni | V | Fe |
| 63 | 0.88 | 0.89 | 7776 | 3868 | 5640 |
| *Particle size distribution, wt%* | | | | | |
| 0–18.9 μm | 18.9–39.5 μm | 39.5–82.7 μm | 82.7–111 μm | > 111 μm | |
| 0 | 7.2 | 49.5 | 24.0 | 19.3 | |