Fe-based Fischer-Tropsch optimization for e-kerosene production

Alessio Tauro[1], Fabio Salomone[1] , Fabrizio Celoria[1], Luca Nodari[2], Luca Romagnoletti[3], Emanuele Felli[4],
Raffaele Pirone[1], Samir Bensaid[1]

[1] Politecnico di Torino, DISAT, Corso Duca degli Abruzzi 24, 10129 Turin (Italy)
[2] Consiglio nazionale delle Ricerche (CNR), ICMATE, C.so Stati Uniti 4, 35127 Padova (Italy)
[3] API Raffineria di Ancona S.p.A., Via Flaminia 685, 60015 Falconara Marittima (Italy)
[4] Italiana Petroli S.p.A., Via Salaria 1322, 00138 Rome (Italy)
E-mail: *fabio.salomone@polito.it*

Introduction. This study advances CO_2-modified Fischer-Tropsch synthesis showing how tailored pre-treatment conditions on a Na-Fe_3O_4 catalyst enhance performance through the formation of active ε'-$Fe_{2.2}C$. The synergy of Mössbauer spectroscopy, Detailed Hydrocarbon Analysis (DHA) and chemometrics tools, such as Principal Component Analysis (PCA), provides outstanding insights into phase transformations and hydrocarbon distributions.

Materials and methods. The Na-Fe_3O_4 catalyst has been tested with different pre-treatment conditions, including activation and carburization at varying temperatures and gas atmospheres, to promote specific iron carbide phases[1]: The activity of the catalysts was tested between 320°C and 380°C, $H_2/CO_2/N_2$: 15/5/3, 7 NL/h/g_{cat}, 360 °C, 23 bar. Characterization techniques such as XRD, Mössbauer spectroscopy, and DHA were employed to evaluate the catalyst's bulk composition, surface properties, and resulting hydrocarbon distributions. Principal Component Analysis (PCA) was applied to DHA data to examine correlations between the hydrocarbon product distribution and the iron carbide phases of the catalyst induced by the pretreatment and the specific reaction conditions (also replicating the composition of a feed deriving from the recirculation of primary unreacted species, i.e. mainly CO and CH_4). The obtained results have been combined with process simulations in order to quantify an e-kerosene cost of production to compare with the traditional Co-based Fischer-Tropsch process within the actual regulatory framework of Sustainable Aviation Fuels (SAFs).

Results and discussion. The results reveal that pre-treatment conditions significantly influence the formation of active iron carbides . Carburization at 400°C proved optimal, promoting ε'-$Fe_{2.2}C$ formation while minimizing α-Fe content, an inactive site for the reaction. The high-temperature carburization (400°C) improved the yield of C_{5+} hydrocarbons, ranging from 14% to 18%, comprising a balanced light-to-heavy oil ratio, while A and AC lead to a predominance of light oil ($T_{cond} < 150°C$). Although the Hägg Carbide (χ-Fe_5C_2) is the main phase often associated with CO_2 conversion activity, other carbides such ε'-$Fe_{2.2}C$ can enhance the catalyst's selectivity for long-chain hydrocarbons and increase the total selectivity to the kerosene range, while shorter-chain olefins were predominant in other pre-treatment samples with lower or no ε'-$Fe_{2.2}C$ content. The combined use of Mössbauer, DHA, and chemometric analysis proved instrumental in identifying active carbide phases and understanding their impact on different reaction pathways.

Keywords: CO_2 Conversion; Fischer-Tropsch; e-fuels; SAF

References: [1] A. Tauro, F. Salomone, F. Celoria *et al. Chem. Eng. J.* **2025**, 515, 163154.