STUDYING PYROLYSIS PRODUCTS OF BOTTOM-OF-THE-BARREL FUEL WITH Py-GCxGC-TOF/CSD/FID

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Bottom-of-the-barrel fuels are expected to play an essential role in the future energy market, primarily due to the lack of practicable and economical alternatives for maritime transportation and power generation. However, these fuels represent a significant environmental threat. Cleaner applications of these fuels require a significant technological leap. Most of the industrial processes employing heavy liquid fuels involve pyrolysis. This work aims to experimentally investigate the major gas products released during Heavy Fuel Oil (HFO) pyrolysis using a pyrolizer, coupled to comprehensive two-dimensional gas chromatography and time-of-flight mass spectrometry (Py-GCxGC-TOF/MS). The 2D data were processed using the GC ImageTM version 2.9 software (Lincoln NE, USA). When a TOF detector is used the software returned three possible molecules, identified as Hint1, Hint2, and Hint3 for each identified peak. Hints are defined according to the NIST/EPA/NIH EI Mass Spectral Library 2.3 version used for peak identification.

A Python-based algorithm has been developed for the data analysis to select the best Hint for each peak and delete all the peaks associated with molecules not realistically present in oil pyrolysis products. The algorithm workflow is reported in Fig1. The SMILES line notation contains comprehensive molecular structure and atomic composition information. Thus, molecules can be classified according to their chemical properties, such as functional groups, molecular weight, stereo-chemistry, and many others. This work classifies peaks according to functional groups and atomic composition. Fig.2 reports the gas product distribution obtained for the HFO.

Data from TOF was confirmed using a Flame Ionization Detector (FID). The qualitative comparison of the 2D chromatogram generated with the two different detectors proved the ability of TOF to identify most of the peaks of the products. Further verification was done for sulfur-containing molecules. The 2D chromatogram returned by Sulfur Chemiluminescent Detector was compared with sulfur-containing molecules classified with the python-based algorithm proving the rightness of the classification.

Small molecules, such as methane, ethane, ethylene, carbon monoxide, carbon dioxide and hydrogen sulfide bypass the GC columns. Thus, the first peak detected by the instrument was resolved in a mixture of the above-mentioned gas using the mass spectrum.
The results presented here represent a significant improvement on what is currently available on the characterization of pyrolysis gas products from bottom-of-the-barrel fuels.

```
Load CAS registry number for the three hints returned by the instrument.
for i in range(Number of Peaks) do
    Convert CAS to SMILE ;
    if Hint1 is suitable then
        Accept Hint1;
    else
        Move to Hint2 ;
        if Hint2 is suitable then
            Accept Hint2
        else
            Move to Hint3 ;
            if Hint3 is suitable then
                Accept Hint3
            else
                Delet row i
            end
        end
    end
end
```

Figure 1. Algorithm workflow

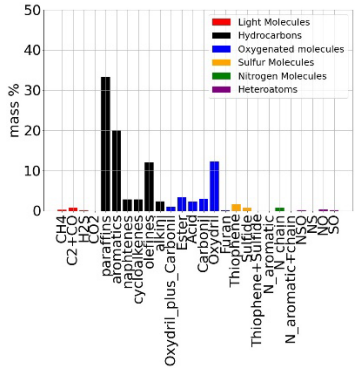

Figure 2. Heavy Fuel Oil pyrolysis gas product distribution.