Co-processing of wood and wheat straw derived pyrolysis oils with FCC feed—Product distribution and effect of deoxygenation

The behavior of bio-oils when co-processed with conventional fossil feed in a fluid catalytic cracking (FCC) unit is suitably tested using a microactivity testing unit (MAT). In the present study, non-catalytic fast pyrolysis oils originating from wood and wheat straw were co-processed in a MAT at a 20/80 weight blend (bio-oil/FCC feed). In addition, bio-oil obtained from deoxygenating the straw derived vapors over a steamed HZSM-5/Al₂O₃ extrudate catalyst was tested. The bio-oils were characterized for elemental composition and moisture content to calculate energy recoveries, amounting to 35% and 30% for the non-catalytically obtained wood and straw oils, while it was 19% for the partly deoxygenated straw oil. Wood oil showed higher acidity (61 mg KOH/g) and molar O/C ratio (0.35) compared to straw oil (54 mg KOH/g and O/C=0.24). The acidity and O/C ratio was reduced for the straw-derived bio-oil from catalytic vapor treatment (3 mg KOH/g, O/C=0.08). At constant conversion (77.5%) at the MAT, the wood pyrolysis oil showed a product distribution quite similar to the reference oil while the wheat straw pyrolysis oil gave a 1.6% points higher coke yield and a 1.2% points lower liquid petroleum gas (LPG) yield. For the catalytically treated wheat straw pyrolysis oil, an even higher coke yield (2.6% points) and 1.9% points lower LPG yield resulted. The observations are attributed to the higher content of aromatics, phenolics, and nitrogen containing compounds of the catalytically upgraded straw fast pyrolysis oil.

Catalytic deoxygenation of vapors obtained from ablative fast pyrolysis of wheat straw using mesoporous HZSM-5

Steam treated HZSM-5 with different Si/Al ratios were tested as catalysts for the upgrading of wheat straw pyrolysis vapors and their performance was compared to hierarchical counterparts, which were prepared by desilication followed by acid washing. Pyrolysis vapors were generated in an ablative system, hot gas filtered, and upgraded in an ex-situ catalyst bed to remove oxygen functionalities and reduce the oils' total acid number (TAN). Besides elemental analysis and TAN, the collected liquids were analyzed for water, chemical composition by gas chromatography mass spectrometry with flame ionization detection (GC–MS/FID), size exclusion chromatography (SEC), thermogravimetric analysis (TGA), and selectively by 1H nuclear magnetic resonance (NMR), 13C NMR, and two-dimensional heteronuclear single-quantum correlation (2D HSCQ) NMR. Hierarchical and conventional catalysts were analyzed with X-ray fluorescence (XRF), ammonia temperature-programmed desorption (NH3-TPD) and ethylamine TPD, N₂ and Ar-physisorption, transmission electron microscopy (TEM) and X-ray diffraction (XRD) to investigate changes induced by the desilication process. In addition, samples were analyzed after several reaction and regeneration cycles to investigate catalyst stability. The hierarchical samples showed an increased coking propensity compared to their parent version. The introduction of mesopores after desilication of HZSM-5 with molar Si/Al ratios of 29 and 39 lead to prolonged activity in deoxygenation and improved carbon recovery in the collected oil fractions compared to the parent counterparts. The results indicate that mild deoxygenation may be a viable way of pretreating pyrolysis oil before co-processing with fossil oil in refineries.
Deoxygenation of wheat straw fast pyrolysis vapors using HZSM-5, Al$_2$O$_3$, HZSM-5/Al$_2$O$_3$ extrudates, and desilicated HZSM-5/Al$_2$O$_3$ extrudates

HZSM-5 extrudates, its two constituents (HZSM-5 zeolite and alumina binder), and SiC for reference were tested after steam treatment for the upgrading of wheat straw fast pyrolysis (FP) vapors from an ablative bench scale system. In addition, mesoporosity was added to the HZSM-5 crystals of the zeolite/Al$_2$O$_3$ extrudates by desilication, which decreased the microporous volume and led to enhanced weak acidity and less strong acidity compared to the parent extrudates. For increasing biomass-to-catalyst ratios (w/w, B:C), oils were collected and analyzed for elemental composition, total acid number (TAN), moisture, molecular weight, evaporation characteristics, and chemical composition by gas chromatography mass spectrometry with flame ionization detection (GC-MS/FID), 1H nuclear magnetic resonance (NMR), 13C NMR, and two-dimensional heteronuclear single-quantum correlation (2D HSQC) NMR. Compared to Al$_2$O$_3$, catalysts containing HZSM-5 promoted aromatization and limited the coke formation due to its shape selective micropores. Nevertheless, Al$_2$O$_3$ was effective in deoxygenation. At B:C ~7, 23 wt-% carbon/25 % energy recovery in the oil fraction was obtained while reducing the oxygen content by 45 % relative to a thermal reference oil fraction obtained over a SiC bed. As such, Al$_2$O$_3$ offers certain benefits compared to HZSM-5 based catalysts due to its lower cost and better hydrothermal stability with respect to acidity. At a catalyst temperature of 500 °C, the introduction of mesopores to HZSM-5 extrudates led to higher energy recovery as oil compared to the parent HZSM-5 extrudates. At B:C = 6.3, 23 wt-% carbon/26% energy recovery in the oil phase was achieved while removing 45% of the oxygen functionalities relative to the thermal reference bio-oil. Compared to deep deoxygenation for direct hydrocarbon production, mild deoxygenation improved the energy recoveries of the oil fractions and appears viable for pretreating pyrolysis vapors before co-processing bio-oils with fossil oil in refineries.
Impact of ZSM-5 Deactivation on Bio-Oil Quality during Upgrading of Straw Derived Pyrolysis Vapors

In this work, we provide detailed information on the change in product distribution and bio-oil quality during extended feeding of biomass derived fast pyrolysis vapors over ZSM-5. The effect of catalyst deactivation by coking on the resulting oil product characteristics was clarified in order to determine when the vapor upgrading should be stopped and the regeneration initiated. Obtaining a stable catalytically fast pyrolysis (CFP) oil while maintaining good energy recovery is important within the context of potential coprocessing of these oils with petroleum feedstocks via fluid catalytic cracking (FCC) or hydrotreatment of the whole CFP oil. Wheat straw derived fast pyrolysis vapors were upgraded in an ex-situ fixed bed reactor containing a steamed ZSM-5 catalyst at 500 °C. Oils were collected both for runs starting the upgrading over a fresh (or regenerated) catalyst and for runs which were continued over an increasingly coked zeolite catalyst. The oils were characterized for water content, elemental analysis, total acid number (TAN), chemical composition by gas chromatography mass spectrometry with flame ionization detection (GC-MS/FID), size exclusion chromatography (SEC), evaporation characteristics by thermogravimetric analysis (TGA), \(^1\)H nuclear magnetic resonance (NMR), \(^{13}\)C NMR, and two-dimensional heteronuclear single-quantum correlation (2D HSQC) NMR. With increasing biomass-to-catalyst mass ratio (B:C), the yield of deoxygenated hydrocarbons decreased, accompanied by a breakthrough of primary pyrolysis vapors leading to an increasing organic liquid yield. The oxygen content of the condensed, phase separated oil fraction increased and the molar O/C ratio of 0.05 and TAN of 6 mg KOH/g for oil collected during B:C = 0–1.1 increased to O/C = 0.18 and TAN = 14 mg KOH/g for oil collected during B:C = 3.6–6.2. Oil produced at 90% reduced catalyst amount and B:C = 0–6.5 and 0–12.9 increased the carbon recovery into the oil product to 23% and 27%, respectively but led to an increase in O/C ratio from 0.18 to 0.22, thus approaching the noncatalytic reference case (SiCbed at 500 °C) of O/C = 0.24. Clear differences in the evaporation behavior of the collected oils were observed, with a shift to more volatile fractions and less charring for products obtained at low B:C ratio. Characterization of the upgraded oils with \(^{13}\)C NMR and \(^1\)H NMR indicated a clear enhancement of thearomatics content and a reduction of sugar and aldehyde compounds. The concentration of carbon within carbonyl, carbohydrates, and methoxy/hydroxy-groups was effectively reduced for oils obtained at low B:C ratios. Catalyst characterization was performed with X-ray fluorescence (XRF), ammonia temperature-programmed desorption (NH\(_3\)-TPD), N\(_2\) and Ar-physorption, transmission electron microscopy (TEM), and X-ray diffraction (XRD). After steaming and four repeated upgrading/regeneration cycles corresponding to an accumulated B:C ratio of 40, the zeolite’s concentration of strong acid sites measured by NH\(_3\)-TPD(T\(_{\text{des}}\) > 275 °C) reduced from 0.43 mmol/g to the calcined version to 0.07 mmol/g and the Brunauer–Emmett–Teller (BET) surface area decreased from 468 to 385 m\(^2\)/g. The hot gas filter upstream of the zeolite bed was found effective in preventing accumulation of potassium on the catalyst.

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Structural, biosynthetic and serological cross-reactive elucidation of capsular polysaccharides from Streptococcus pneumoniae serogroup 18
Capsular polysaccharides (CPS) are crucial virulence factors of Streptococcus pneumoniae. The previously unknown CPS structures of the pneumococcal serogroup 16 (serotype 16F and 16A) were thoroughly elucidated by nuclear magnetic resonance (NMR) spectroscopy and verified by chemical analysis. The following repeat unit structures were determined:

16F: \(-3)-\alpha-L-Rhap\-[4-P-1-Gro\]-\(1-3\)-\(\alpha-D-GlcP\)-[\(6-P-1-Gro\)]\-(1-3)-\(\beta-L-Rhap\)-[2-OAc\]-\(1-4\)-\(\beta-D-GlcP\)-\(1\)

16A: \(-3)-\beta-D-Galf\-[2-OAc\]-\(1-3\)-\(\alpha-L-Rhap\)-(1-2)-\(\alpha-L-Rhap\)-(1-3)-\(\alpha-D-Galp\)-[\(6-P-1-Gro\)]\-(1-3)-\(\beta-D-Galp\)-(1-4)-\(\beta-D-GlcP\)-\(1\)

70% OAc: O-acetyl substitution; P-1-Gro: glycerol-1-phosphate substitution.

A further analysis of CPS biosynthesis of serotype 16F and 16A, in conjunction with published cps gene bioinformatics analysis and structures of related serotypes, revealed presumable specific function of glycosyltransferase, acetyl transferase, phosphotransferase and polymerase. The functions of glycosyltransferase WcxN and WcxT were proposed for the first time, which were assigned to catalyze linkage of \(\alpha-L-Rhap\)-\(1-3\)-\(\alpha-D-GlcP\) and \(\alpha-L-Rhap\)-\(1, 2\)-\(\alpha-L-Rhap\), respectively. Furthermore, since serotype 16F was genetically close to serogroup 28, cross-reactions between serogroup 16 and serogroup 28 were studied using diagnostic antisera, which provided further understanding of antigenic properties of CPS and diagnostic antisera. Interestingly, serotype 16F cross-reacted with factor antisera 28b and 11c. Meanwhile, serotype 16A cross-reacted with factor antiserum 11c.

Importance: The vaccine pressure against Streptococcus pneumoniae could result in the change of prevalence in carriage and invasive serotypes. As such, it is necessary to monitor the distribution to achieve successful vaccination of the population, and similarly, it is important to increase the knowledge of even the currently less prevalent serotypes. The CPS are vital for the virulence of the pathogen and antigenic properties of CPS are based on the structure. Consequently, a better understanding of the structure, biosynthesis and serology of the capsular polysaccharides can be of great importance towards developing future diagnostic tools and vaccines.

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