Production of Upgraded Bio-oils from Miscanthus Acid Hydrolysis Residues by Catalytic Pyrolysis – Effect of Feed and Acid Hydrolysis Conditions

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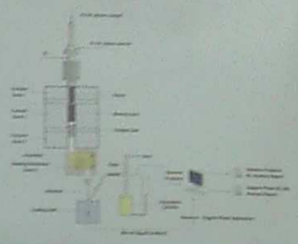
Introduction

In this study we investigated the upgrading of acid hydrolysis residues (AHRs) through thermal and catalytic pyrolysis. The AHRs were by-products from a AH process developed in the U. Limerick (UL) for levulinic acid production. The AHRs originated from the AH process performed under different operating conditions (severities). The severity reflects the temperature and acid concentration of the hydrolysis process. The objective of this work was to examine how the severity of the AH process affects the potential of using AHR as pyrolysis feed.

Experimental

The pyrolysis of AHRs with the catalytic materials was performed at 500 °C, using a bench-scale fixed bed reactor, made of stainless steel 316 and heated by a 3-zone furnace. The catalyst bed temperature was used as the experiment temperature and it was monitored with a thermowell. A specially designed piston system was used to introduce the biomass feedstock into the reactor. A constant stream of N_2 was fed from the top of the reactor for the continuous withdrawal of the products and the maintenance of the inert atmosphere during pyrolysis. The products condensate in a glass receiver submerged in a cooling bath kept at -17 °C. Non-condensable gases were collected in a gas collection system. For each run, 1.5 g of feed and 0.7 g of catalyst were required.



Materials

Seven AHRs were used in this work. These samples were produced in UL after acid hydrolysis of Miscanthus at different severities (temperature, acid concentration). The samples were fully characterized in CPERI (Tables I, II) and the code names (sev-1 to sev- 7) declare an increased hydrolysis severity order.

Table I: Elemental analysis of dry AHRs

	C	H	O	Ash
Miscanthus	48.2%	5.9%	44.6%	2.7%
sev-1	47.6%	5.3%	46.4%	0.7%
sev-2	49.0%	6.1%	44.0%	0.9%
sev-3	55.2%	5.7%	37.4%	1.3%
sev-4	63.6%	5.1%	31.3%	5.1%
sev-5	65.1%	5.1%	28.2%	1.7%
sev-6	67.4%	4.7%	23.0%	1.7%
sev-7	69.3%	4.8%	23.3%	1.5%

Table II: Biomass constituents content of dry AHRs

	Extract.	Lignin	Cel.	Hemicel.
Miscanthus	1.3%	26.5%	40.4%	29.1%
sev-1	4.1%	24.8%	32.9%	38.1%
sev-2	5.3%	25.3%	29.4%	40.5%
sev-3	5.7%	37.0%	26.7%	29.3%
sev-4	6.9%	93.9%	n.a.	n.a.
sev-5	7.2%	79.7%	n.a.	n.a.
sev-6	4.8%	86.8%	n.a.	n.a.
sev-7	6.5%	92.3%	n.a.	n.a.

With AH treatment, the cellulose and hemicellulose contents of Miscanthus decreased and lignin residue was produced. Higher lignin results in higher Carbon and lower Oxygen content in the AHR.

Silica sand and a commercial ZSM-5 were used for the pyrolysis tests. The Silica sand was an inert material with no surface area and no acidity, while the commercial ZSM-5 is suggesd in the literature as a promising catalyst for the deoxygenation of biomass and aromatics production. The ZSM-5 catalyst had a total surface area (TSA) of 138 m^2/g, an average pore diameter of 4 nm and microporosity and mesoporosity of 0.037 and 0.150 cm^3/g respectively.

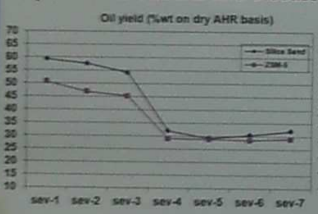
Product Characterization

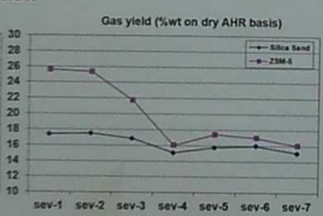
- **Cracked Gases:** By GC (CO_2, CO, HC)
- **Bio-oil:** ASTM E203-08 (H_2O), ASTM D5291 (C, H)
- **Organic fraction:** GC/MS, GCxGC-TOFMS
- **Aqueous fraction:** GC-FID
- **Solids:** ASTM D5291 (C, H analysis)

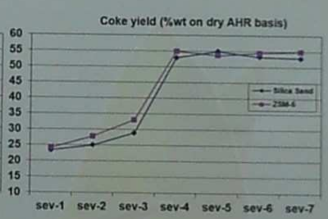
Bio-oil is composed of hundreds of compounds. Classification in 14 basic groups aims at better understanding and easier assessment of the process.

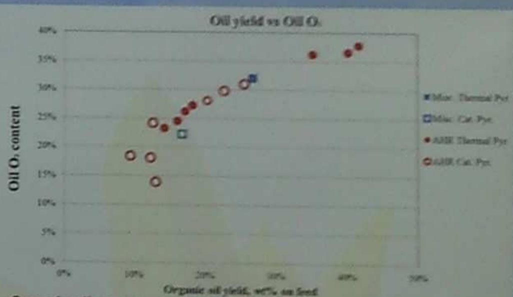
Desirable		Undesirable	
AR	Aromatic HC	AC	Acids
ALI	Aliphatic HC	ALD	Aldehydes
PH	Phenols	KET	Ketones
FUR	Furans	PAH	Polyaromatic HC
AL	Alcohols	UN	Unidentified

Experimental Results and Discussion









Thermal Pyrolysis

The AH severity affects strongly the behavior of AHRs. As the severity increases, both hemicellulose and cellulose tend to be solubilized leaving an AHR rich in lignin that is less crackable and gives high coke and low bio-oil yields. The AHR from the most severe AH conditions gives almost 55%wt coke and 30%wt bio-oil. The gas yield is only slightly affected by the severity of the AHRs and it is around 15-17%wt. Among these gases the CO_2 and the CO dominate with the CO_2 yield to be around 10%wt.

Catalytic Pyrolysis

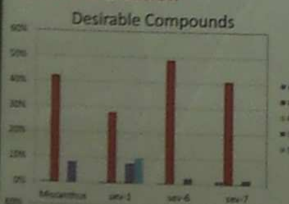
The catalytic pyrolysis plays a more important role when a low severity AHR is used as pyrolysis feed. For high severity AHRs the catalytic effects are less important. The catalytic upgrading increases gases, coke and H_2O yields. In contrast with thermal pyrolysis, the CO is the dominant gas from the catalytic tests. The oil yield is reduced in all cases. It seems that catalytic pyrolysis of AHRs favors the deoxygenation via CO, CO_2 and H_2O and decreases the bio-oil yield, but improves its quality by producing a bio-oil with less O_2.

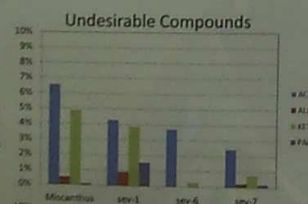
Organic oil vs. oxygen in organic oil

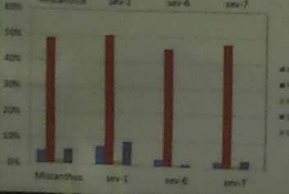
Thermal pyrolysis: low severity AHRs give about 40%wt organic oil with 35%wt O_2. The high severity AHRs give 15-25%wt organic oil with 25%wt O_2.

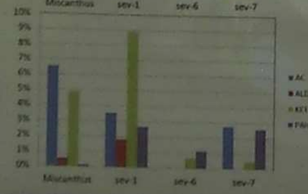
Catalytic pyrolysis: low severity AHRs give about 20-25%wt organic oil with 30% O_2. The high severity AHRs give less than 15%wt organics. For these AHRs the severity plays an important role in the oil deoxygenation (O_2 content from 15-25%wt)

GC-MS Evaluation









Miscanthus and sev-1 AHR produce a large variety of chemical compounds. Phenols were mostly attributed to the degradation of lignin while ketones, acids and sugars were mostly cellulose and hemicellulose pyrolysis products.

Increasing AH severity (sev-6 and sev-7) resulted in lignin derivatives (Phenols) production.

In the case of catalytic pyrolysis, the cellulose/hemicellulose derivatives were cracked, some yielding hydrocarbons, while phenols appeared to be unaffected by catalysis.

Conclusions

- Low severity AH treatment → AHR rich in cellulose and hemicellulose.
- Higher severity AH treatment → lignin-rich AHR.
- Severe AH treatment → low bio-oil yield from AHR thermal pyrolysis, with decreased O_2 content.
- Catalytic pyrolysis is important in low severity AHRs. In general it enhances bio-oil de-oxygenation but gives less bio-oil yields
- Bio-oil composition is strongly dependent on the AH treatment. Cellulose/hemicellulose-rich AHRs produce products like Ketones, Furans, Alcohols and Acids.
- Lignin-rich AHRs selectively produce Phenols.
- High severity AH treatment yields coke-like AHRs that can give in the pyrolysis process less than 15% organic oil and 55%wt coke.

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