1. **Novel Solid Acid and Base Catalysts (Aim 3.1)**
   Approach: Solid oxide solutions
   2-methyl-3-butyn-2-ol conversion as test reaction
2. **Probing Sites and Prediction of Reactivity (Aims 3.2 and 3.3)**
   Concept and methodology: IR absorption coefficients
   Propene activation on zeolites
3. **Catalyst-Adsorbate Interactions (Aim 3.3)**
   Bifunctional reactants
   IR spectroscopy and calorimetry
4. **Thermal Analysis of Switchgrass Pyrolysis (Aim 3.4)**
   TG-MS-FTIRS experiments

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Oklahoma EPSCoR Retreat
Ardmore, OK – July 14, 2010

Catalyst-Adsorbate Interactions (Aim 3.3)

Volatile pyrolysis products

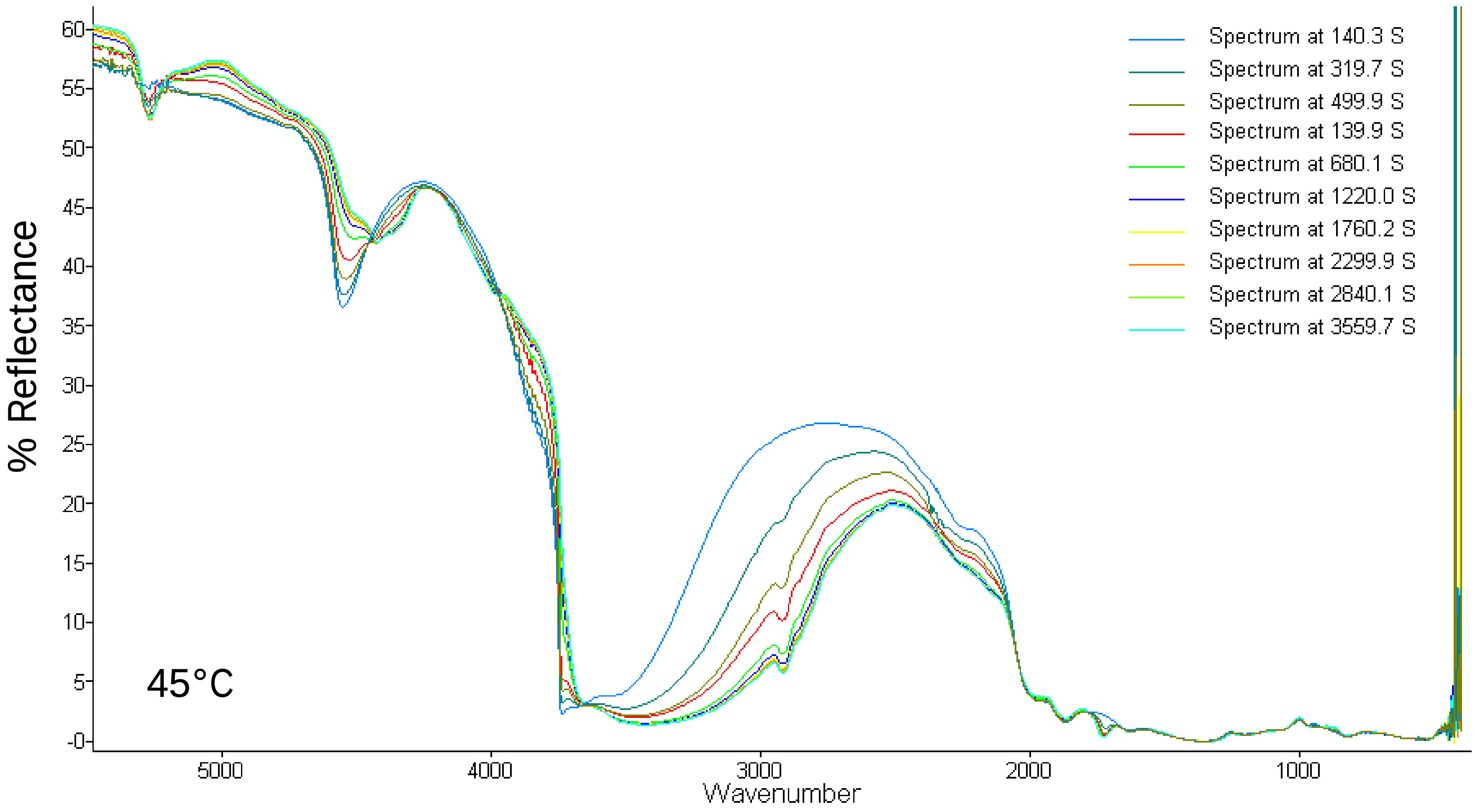
Compound	Switchgrass		Sweet sorghum		Corn stalk		Poplar		Cellulose	
	Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD
Formaldehyde	1.0	47	0.57	46	0.5	50	0.8	62	1.6	24
Methanol	0.66	36	0.46	40	0.8	49	1.3	51	0.22	35
Acetaldehyde	0.50	44	0.35	15	0.4	33	0.40	9	0.43	41
Glyoxal	5.8	74	2.2	47	3.2	86	2.7	61	5.1	5
Acetone	0.35	51	0.3	50	0.42	56	0.26	79	0.48	24
Methylglyoxal	5.0	52	3.8	71	5.1	74	2.7	45	2.8	25
Hydroxyacetaldehyde	14	36	14	53	12	63	12	37	7.4	22
Acetic acid	2.9	32	3.6	85	5.0	68	5.2	56	0.18	42
3-pentanone	1.1	96	1.6	59	2.1	86	1.5	48	0.40	8
Hydroxyacetone	2.1	60	2.2	83	3.7	86	2.4	88	0.20	33
Acetoxy-acetaldehyde	2.6	63	2.9	55	3.3	87	3.8	68	0.09	62
Butandial	2.7	75	3.5	53	2.9	69	4.9	68	n.d.	
Sum	38	42	35	50	39	66	38	46	19	10

Mean values and % relative standard deviations (n = 5).

- Adsorption of hydroxyacetone on various oxides (typical catalyst supports)
- Infrared spectroscopy: investigate adsorbate structure and temperature-programmed desorption and reaction
- Adsorption calorimetry: differential heats of adsorption

C. Torri, D. Fabbri, Microchemical Journal 93 (2009) 133–139

Hydroxyacetone Adsorption on Silica



- Si-OH groups on the surface of the oxide interact with hydroxyacetone

NSF-MRI Equipment

1. **TG-MS-FTIRS: Thermogravimetry with differential thermal analysis or differential scanning calorimetry and evolved gas analysis by mass spectrometry and FTIR spectroscopy**
    - NETZSCH STA 449 F1 Jupiter / MS 403 C Aëolos / Bruker Tensor 27
    - Maximum temperature of thermobalance: 1500°C; digital resolution 0.025 µg; maximum sample load/measurement range 5 g including sample crucible

2. **Mixing and Reaction Calvet calorimeter**
    - SETARAM C80
    - Resolution 0.1 µW; temperature ambient to 300°C; various vessels for calorimetric experiments
    - To be combined with Micromeritics ASAP 2020 gas dosing apparatus for measurements of differential heats of adsorption

Thermal Analysis of Switchgrass Pyrolysis (Aim 3.4)

- CBME/OU operates two pyrolysis units, one large scale (0.5-2 kg solid feed/h) and one small scale (g/h) unit
- Large variety of switchgrass samples received from Samuel Roberts Noble Foundation
- Product distribution depends on properties of feedstock and pyrolysis conditions, which may vary locally because of heat and mass transfer limitations in the reactor
- Switchgrass decomposition in the TG-MS-FTIRS apparatus: small sample size in the milligram range allows for better control over the conditions than in the larger pyrolysis units
- Influence of feedstock composition, heating rate, holding temperature, and the addition of catalysts