University of Idaho
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Upgrading Agricultural Mixed Plastic And Lignocellulosic Waste To Fuels By Catalytic Pyrolysis

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Abstract

Agriculture generates non-recyclable mixed waste streams, such as plastic (e.g., netting, twine, and film) and crop residues (e.g., chaff and bluegrass). Agricultural mixed waste (AMW) is currently disposed by incineration or landfilling. Thermochemical conversion technologies, such as pyrolysis, offer an option to upcycle this waste into transportation fuel. In this work, AMW is homogenized by compounding in a twin-screw extruder and characterized by thermal analysis. The homogenized AMW is thermally and catalytically pyrolyzed (500-600 °C) in a tube batch reactor and the liquid products are collected and characterized using a combination of FTIR, GCMS and ESI-MS. The chemical characteristics of the solid char product are characterized by FTIR spectroscopy. Thermal pyrolysis products mainly comprise straight-chain hydrocarbons, and catalytic pyrolysis products comprise short-chain hydrocarbons and aromatics. The results show a high degree of similarity between the chemical profiles of catalytic pyrolysis products and gasoline.

Methodology

Agricultural mix waste collected from Idaho farms

Bluegrass Mix Plastic (BMP) and Chaff Mix Plastic (CMP) were compounded by twin screw extrusion, granulated, and re-extruded to obtain a homogeneous extruded material.

Characterization Techniques and Methods

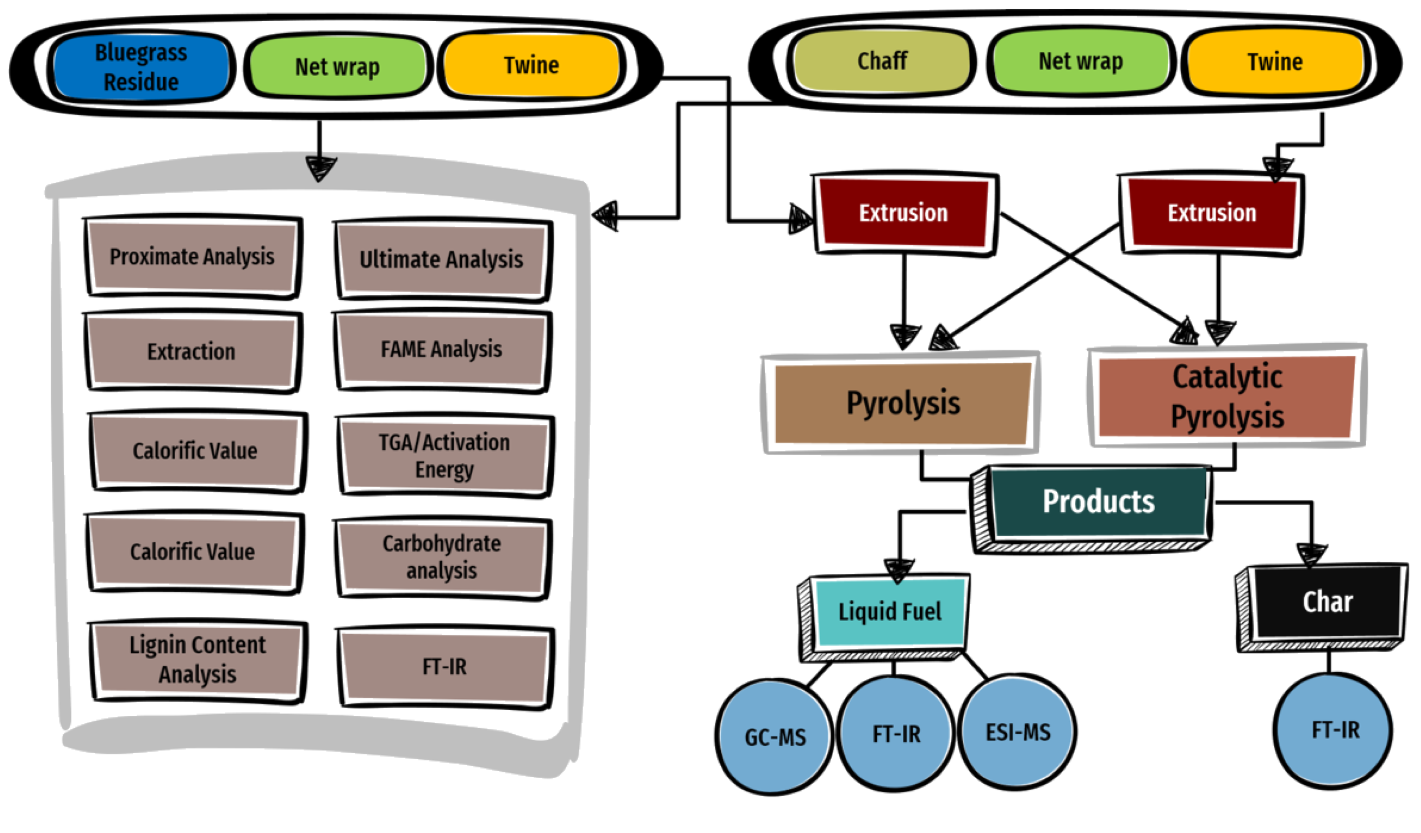

Figure 1: Research methodology flowchart

Pyrolysis

BMP and CMP are pyrolyzed in a custom-built batch reactor (**Figure 2**) at 500, 550, and 600 °C with and without zeolite Y catalyst.

The substrate (1 gram) is sandwiched between glass wool and zeolite Y on both sides and the end secured with glass wool

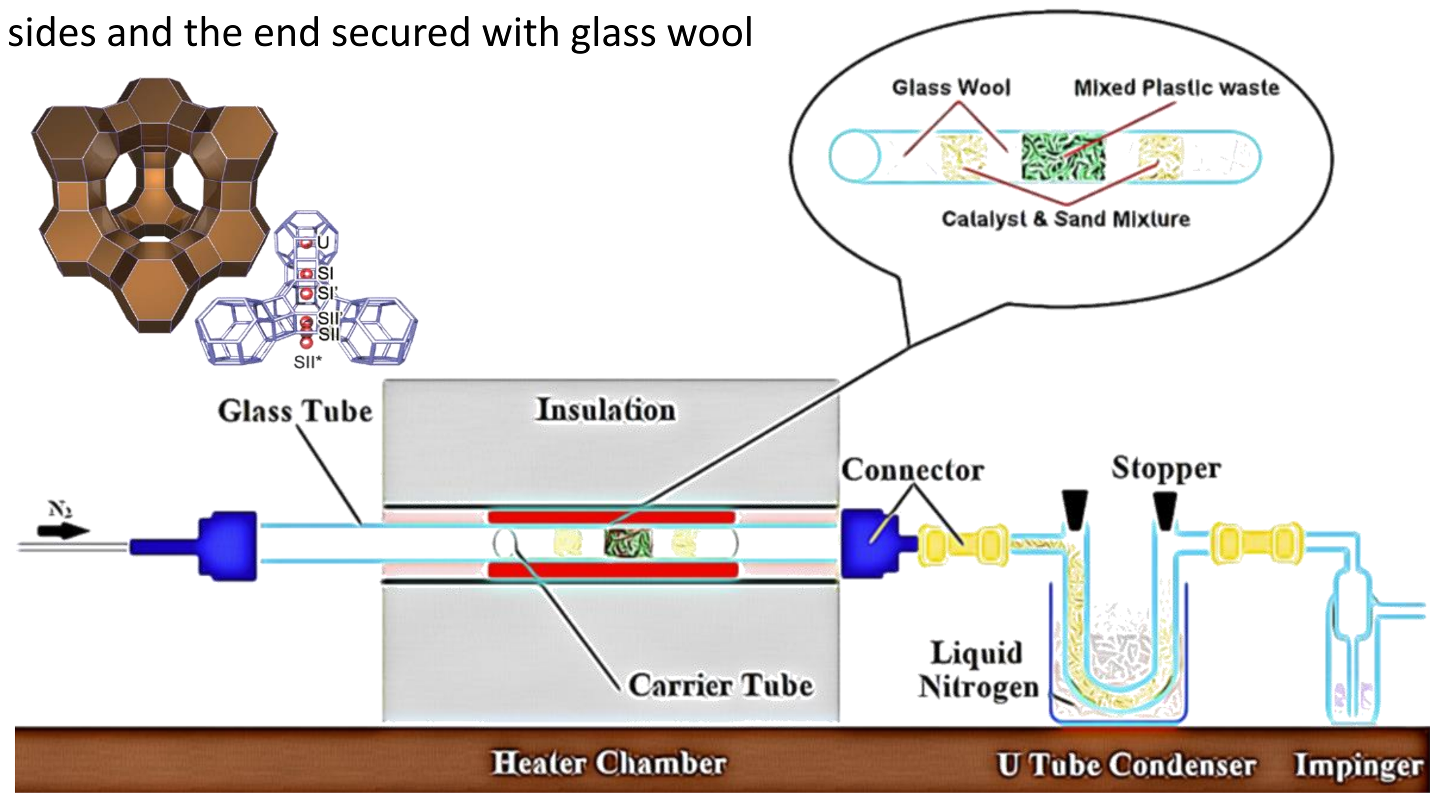

Figure 2. Schematic representation of the pyrolysis reactor and Zeolite Y 3D framework.

Results

Table 1. Proximate and ultimate analyses, density, calorific values, and chemical content of bluegrass, chaff, mixed plastic, BMP, and CMP.

	Bluegrass	Chaff	MP	BMP	CMP
% N	1.2 ± 0.04	1.2 ± 0.06	0.9 ±0.03	0.3 ± 0.02	0.4 ±0.01
% C	37.0 ± 1.8	32.2 ± 1.6	74.2 ± 2.9	69 ± 3.1	72.7 ± 3.5
% Ash	17.1 ± 0.8	5.46 ± 0.26	1.02 ± 0.04	3.73 ± 0.17	5.9 ± 0.27
% Fixed Carbon	21 ± 0.9	15.5 ± 0.7	0	8.1 ± 0.4	5.3 ± 0.25
% Volatile Matter	61.9 ± 1.3	71 ± 0.9	98.98 ± 0.3	88.17 ± 0.5	89 ± 0.8
Density	1.45 ± 0.07	1.34 ± 0.03	0.95 ± 0.02	1.09 ± 0.01	1.04 ± 0.04
Calorific Value (MJ kg^{-1})	19.7 ± 0.4	17.5 ± 0.2	46.2 ± 0.9	35.4 ± 0.3	39 ± 0.2
% Lipid (Extractive)	2.1 ± 0.3	3.2 ± 0.5	-	-	-
% Structural Carbohydrate	55 ± 1.8	58 ± 0.6	-	-	-
% Lignin Content	22.98 ± 0.5	23.6 ± 0.23	-	-	-

- Density used to identify the ratio of lignocellulosic content (L) to plastic (P) in each feed stock. L:P was 16.8:83.2 in CMP and 36.2:63.77 in BMP.
- **FAME:** palmitic acid (C16:0), linoleic acid (C18:2b), and oleic acid (C18:1) are most abundant fatty acid methyl esters in both bluegrass and chaff samples.

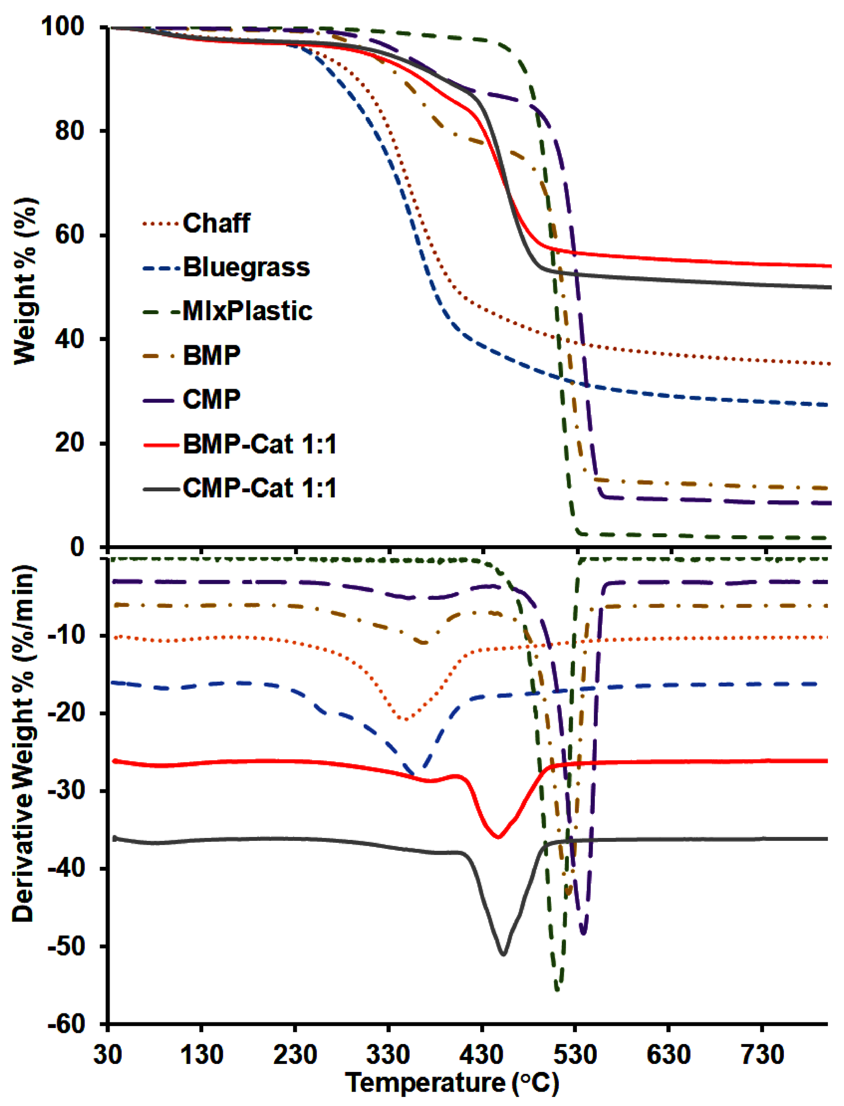

Figure 3. TGA and DTG thermograms of chaff, bluegrass, mix plastic, BMP, CMP, BMP-Cat, and CMP-Cat.

- Shift in degradation stages observed by using catalyst (**Figure 3**):
  - Catalyst lowers degradation temperatures by about 85 °C in BMP and 91 °C in CMP.
  - FWO method: catalyst decreases average activation energy from 209 J/mol to 181 in BMP and 203 to 187 J/mol in CMP.

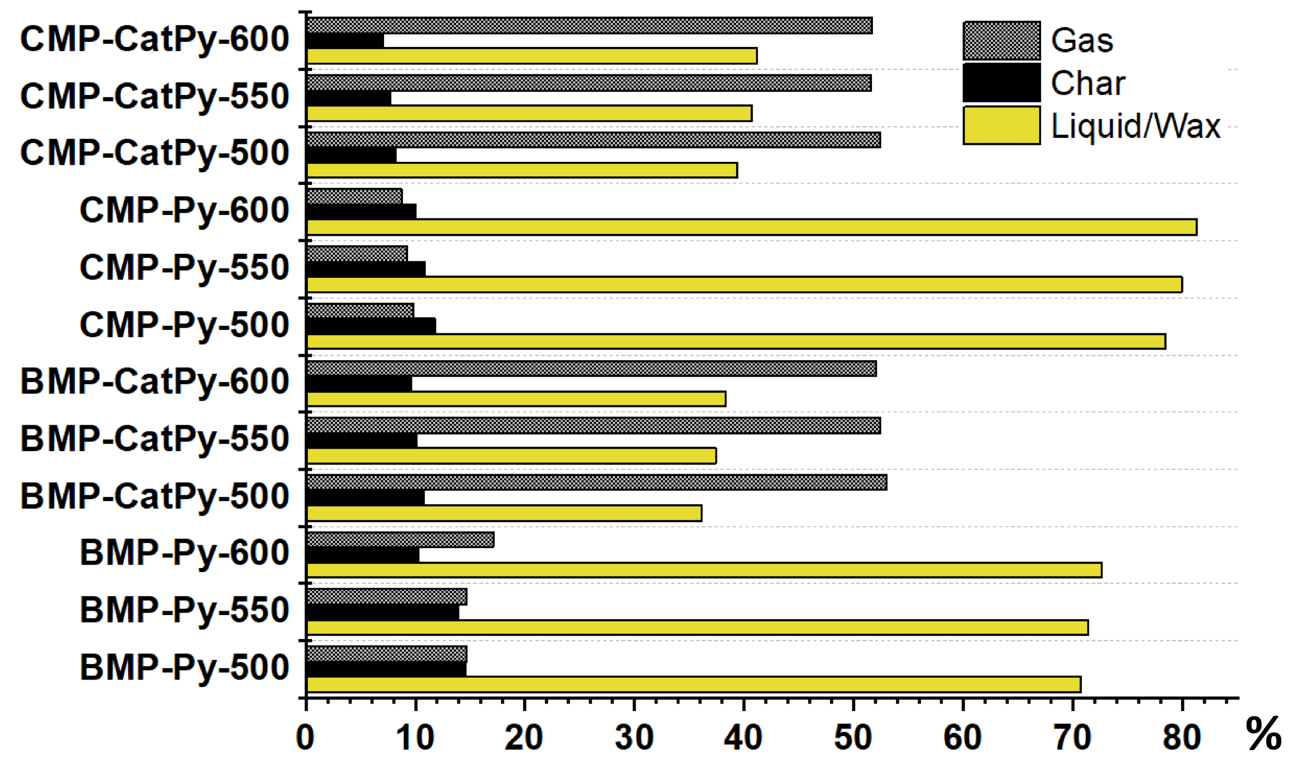

Figure 4. Pyrolysis and Cat-Pyrolysis product yields at 500, 550, 600 °C.

- Liquid/Wax yield is correlated with temperature in both thermal and catalytic pyrolysis.
- Highest liquid/wax yield occurs at 600 °C in CMP pyrolysis.
- Highest liquid yields are 81% and 41% for thermal and catalytic pyrolysis, respectively.

Results

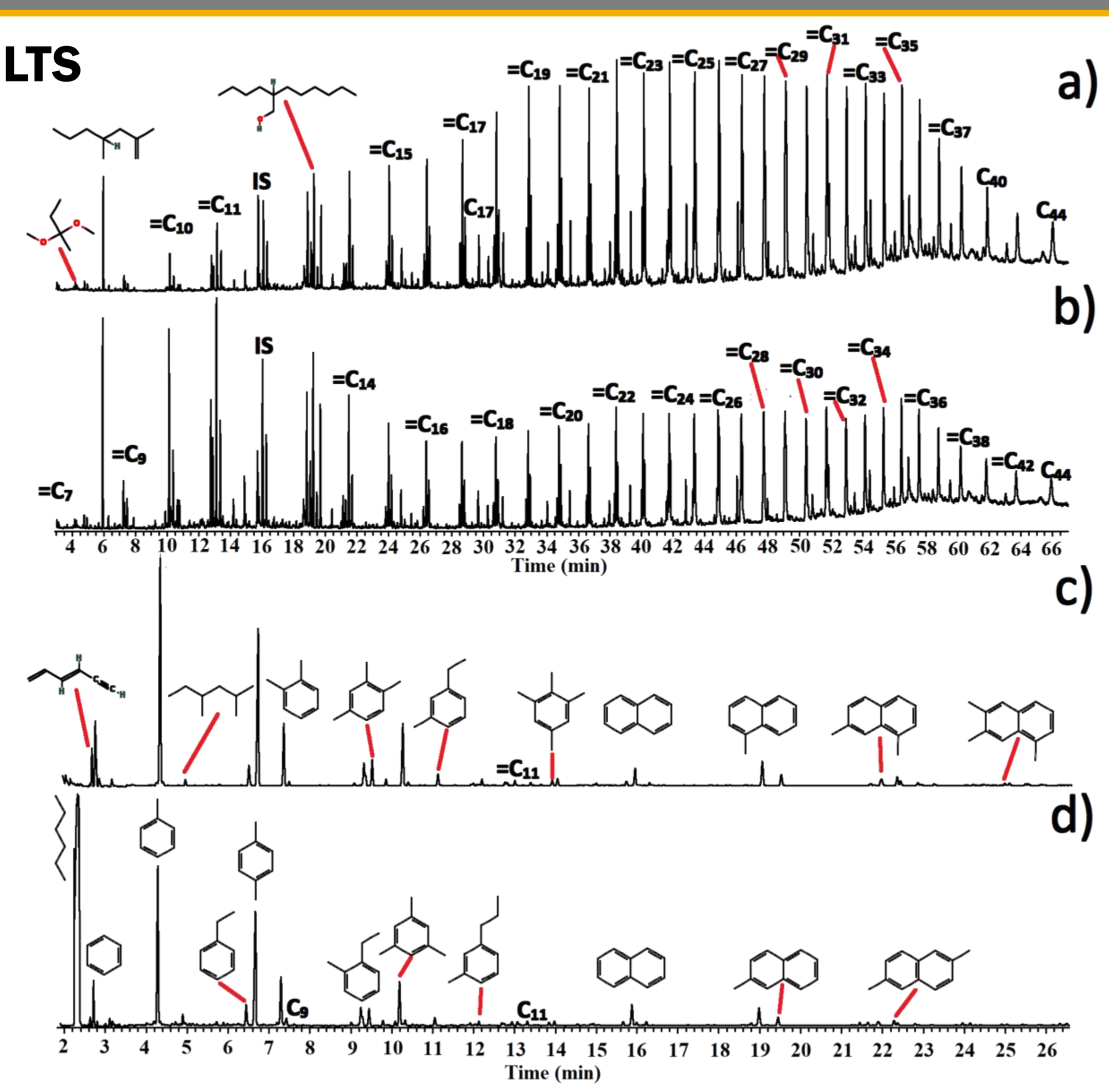

Figure 5. GC-MS of (a) CMP-Pyro-600, (b) BMP-Pyro-600, (c) CMP-CatPyro-600, (d) BMP-CatPyro-600.

- The wax product is made of long-chain alkanes, olefins, dienes (C_7-C_{44}), aromatics (0.63%), and oxygenated compounds (12.3%).
- The liquid product from catalytic pyrolysis is a mixture of aromatics (C_6-C_{13}), alkanes (C_6-C_8), and alkenes (C_6-C_{21}).
- ESI-MS results show that the molar mass of all samples decreased by an average of 10% in BMP and 7% in CMP after catalytic pyrolysis. A decrease in average molar mass is the result of thermal degradation and samples' reaction with the catalyst.

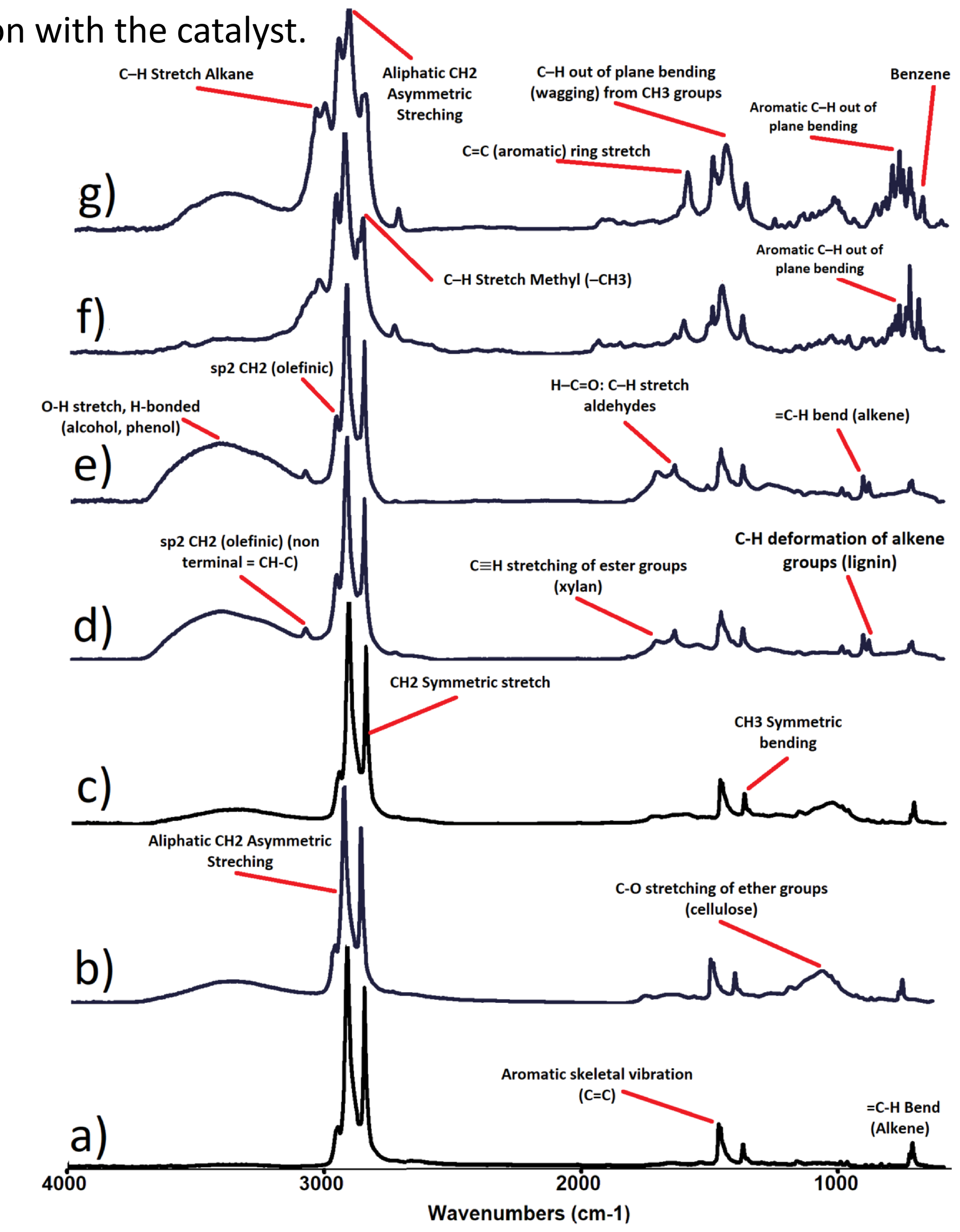

Figure 6. FTIR of (a) mix plastic, (b) CMP, (c) BMP, (d) CMP-Pyro-600, (e) BMP-Pyro-600, (f) CMP-CatPyro-600, (g) BMP-CatPyro-600(g).

Conclusion

Zeolite Y facilitates the breakdown of long chain hydrocarbons into short-chain alkanes and aromatics. The wax product of thermal pyrolysis is less suitable as fuel due to the absence of aromatic compounds and the presence of oxygenated compounds. The profile of aromatics in catalytic pyrolysis liquid products was chemically and functionally identical to gasoline, making it suitable for use as a "drop-in" gasoline fuel. The catalyst may be recovered and reused.

Acknowledgements

This work is supported by AFRI Grant NF5330 from the USDA National Institute of Food and Agriculture. We would like to also acknowledge the College of Natural Resources in the purchase of the GC-MS.