

ABSTRACT

Lignin, a complex and abundant natural polymer, is the promising raw material as a renewable source for the production of high-value aromatic compounds. However, the efficient depolymerization of lignin remains a formidable challenge, and hydrogen is required in the process. This study was performed by combining lignin hydrothermal liquefaction (HTL) and glycerol aqueous phase reforming (APR). The APR process produces hydrogen by reacting glycerol with water, eliminating the need for an external hydrogen source. Using glycerol as the hydrogen source, we achieved significant yields of valuable aromatic compounds, including syringol, guaiacol and catechol. Overall, this study sheds light on the potential of process integration of APR and HTL to promote lignin valorization and offers new avenue for sustainable biomass into valuable chemicals. It is also expected to have important implications for ways to utilize crude glycerol, a by-product of the biodiesel industry.

Keywords: Hydrothermal liquefaction, lignin, depolymerization, aqueous phase reforming, glycerol, hydrogen, bio-oil

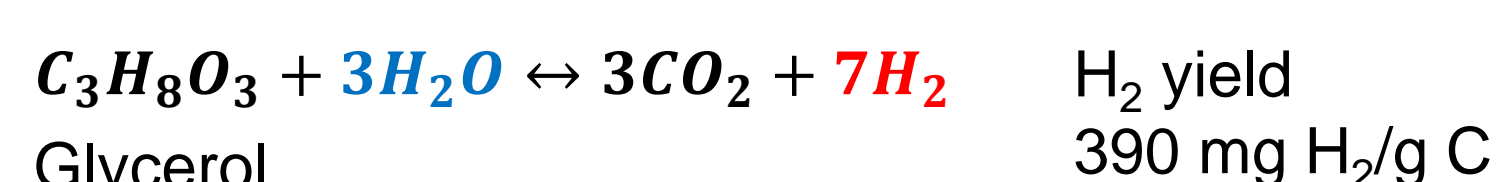
Introduction

Background

Lignin is a complex and abundant natural polymer found in lignocellulosic biomass, making it a promising renewable source for the production of high-value aromatic compounds. However, efficient depolymerization of lignin is challenging and requires hydrogen.

Glycerol aqueous phase reforming (APR) is a process that reacts glycerol, a by-product of biodiesel production, with water to generate hydrogen. In this process, glycerol undergoes reforming in the presence of water and a catalyst, producing hydrogen gas along with carbon dioxide and other by-products. This process can internally produce hydrogen without the need for an external supply, which can then be used to facilitate lignin hydrothermal liquefaction (HTL), making the overall process more economical.

<Glycerol aqueous phase reforming (APR)>



Objectives

- To integrate APR and HTL processes for efficient depolymerization of lignin and production of aromatic compounds.
- To optimize hydrogen supply and depolymerization using Pt/C, Ru/C, and Raney Ni catalysts.
- To achieve significant yields of aromatic compounds such as syringol, guaiacol, and catechol, and enhance the utilization of glycerol, a by-product of biodiesel production.

Materials & Methods

Raw material

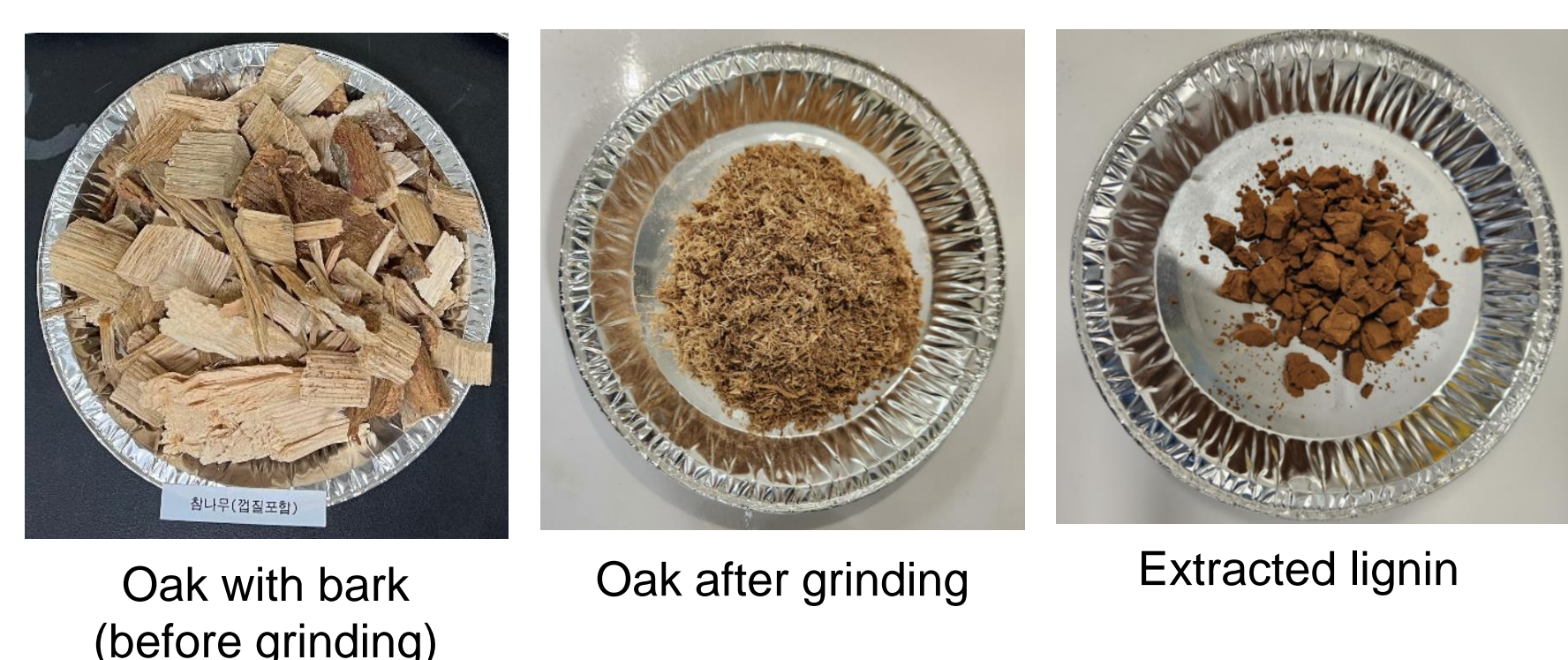
Unused forest biomass oak (including bark)

Unused forest biomass from oak, including the woody parts with bark, was supplied by Kookmin University.

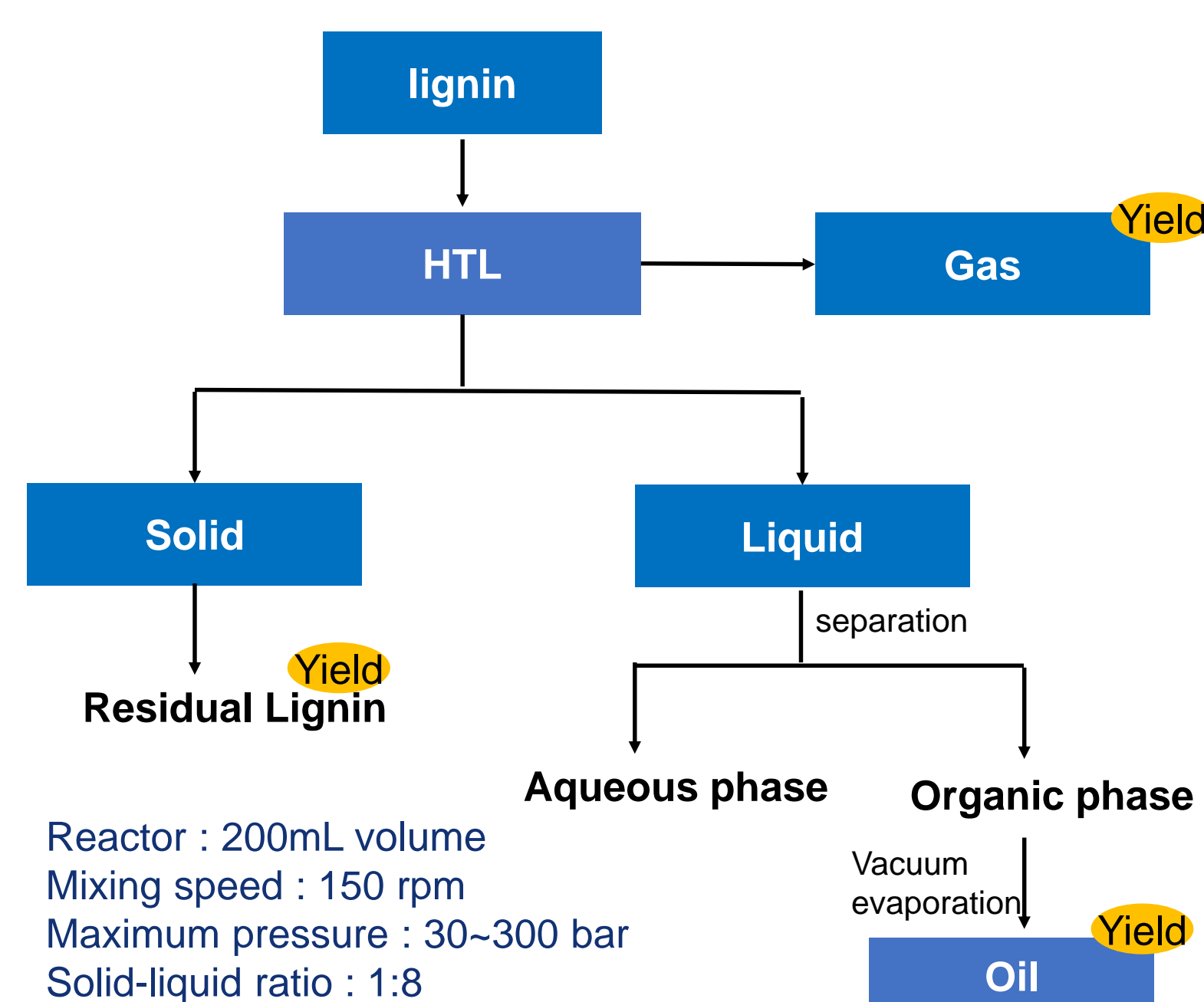
Lingin extraction

Organosolv Ligin

Lignin extraction was performed using the Parr 4600 reactor with a volume of 1 L. The organosolv pulping was used a mixture of ethanol-water (30/70, 40/60, 50/50, 60/60 w/w), with sulfuric acid (H₂SO₄) as a catalyst (1.2 % w/w). The treatment was carried out at 170 °C with controlled to an H-factor of 1100 and the solid to liquid ratio was 1:8 (w/w). Dissolved organosolv lignins were isolated by precipitation with two volumes of cold water. The organosolv lignin was recovered by filtration and then dried at 45 °C for 24 hours.



Hydrothermal liquefaction (HTL)



no.	Solvent	Time	Temp.	Catalyst
1			250°C	
2			300°C	
3			350°C	
4			400°C	
5			250°C	
6			300°C	Pt/C
7			350°C	Pt/C
8	Glycerol	30 min	400°C	
9	10%		250°C	
10			300°C	Ru/C
11			350°C	Ru/C
12			400°C	Ru/C
13			250°C	
14			300°C	Raney Ni
15			350°C	Raney Ni
16			400°C	Raney Ni

After mixing 8g of lignin and 80mL of solution with a catalyst (5 wt%), the mixture was stirred at 150rpm at the target temperature (250, 300, 350, 400°C) and reacted for 30 minutes. After the reaction was complete, the slurry-like product in the container was recovered using ethyl acetate and filtered to separate the solid residual lignin and the liquid. The solid was then dried in an oven at 55°C, and the liquid was processed with a rotary evaporator to remove the ethyl acetate. Finally, the yield was calculated.

Analysis

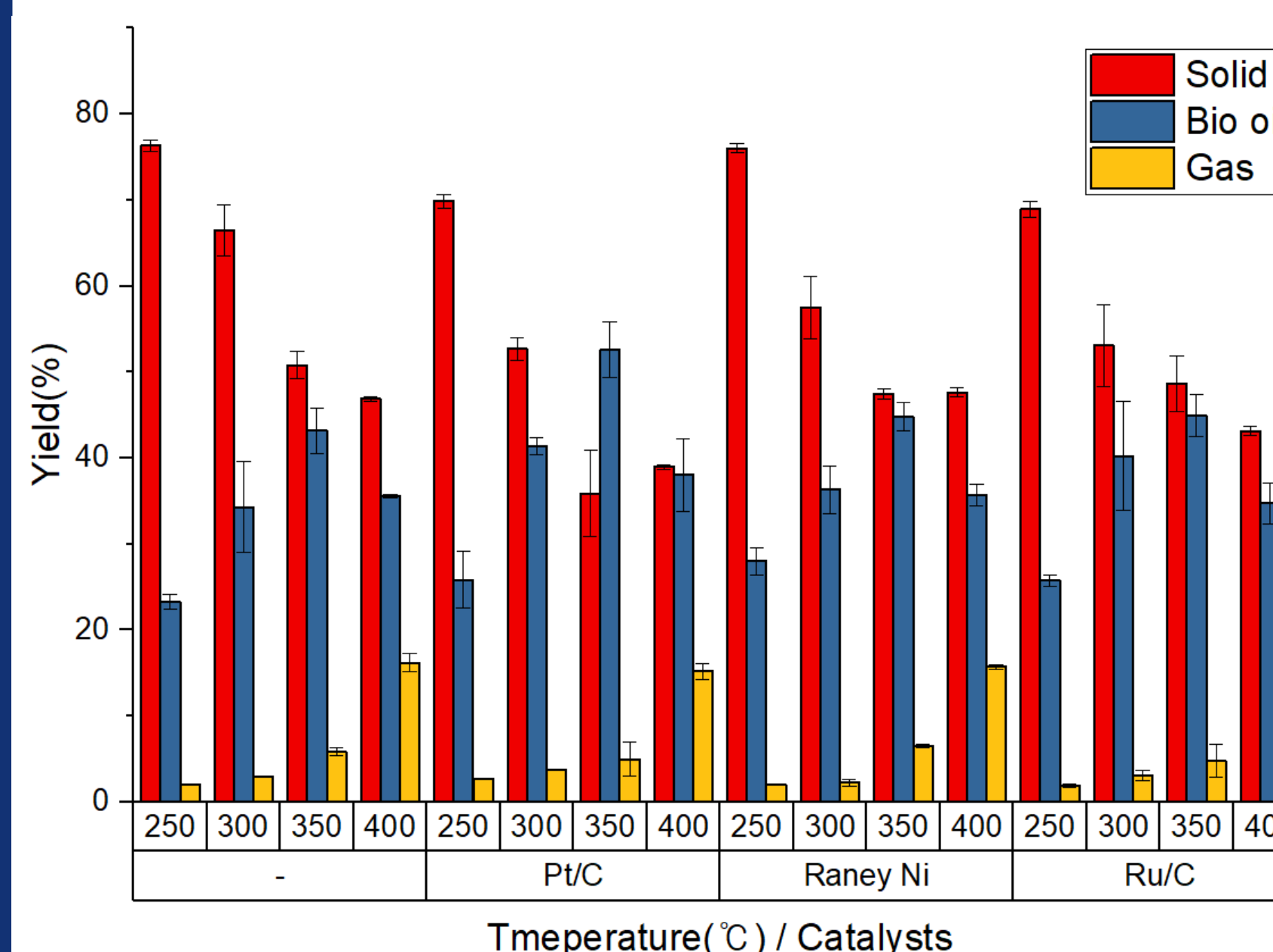
- Fourier-transform infrared spectroscopy : FT-IR
- Thermo-Gravimetric Analysis: TGA
- Gas Chromatography-Mass Spectrometry : GC-MS
- Gas Chromatography : GC

The characteristics of the bio-oil produced under each condition were analyzed using GC-MS, FTIR, and TGA. The gases generated after the reaction were analyzed using GC to determine the hydrogen content, and the effectiveness of glycerol aqueous phase reforming.

Results & Discussions

Yield of the HTL products

Influence of Temperature and Catalyst Type

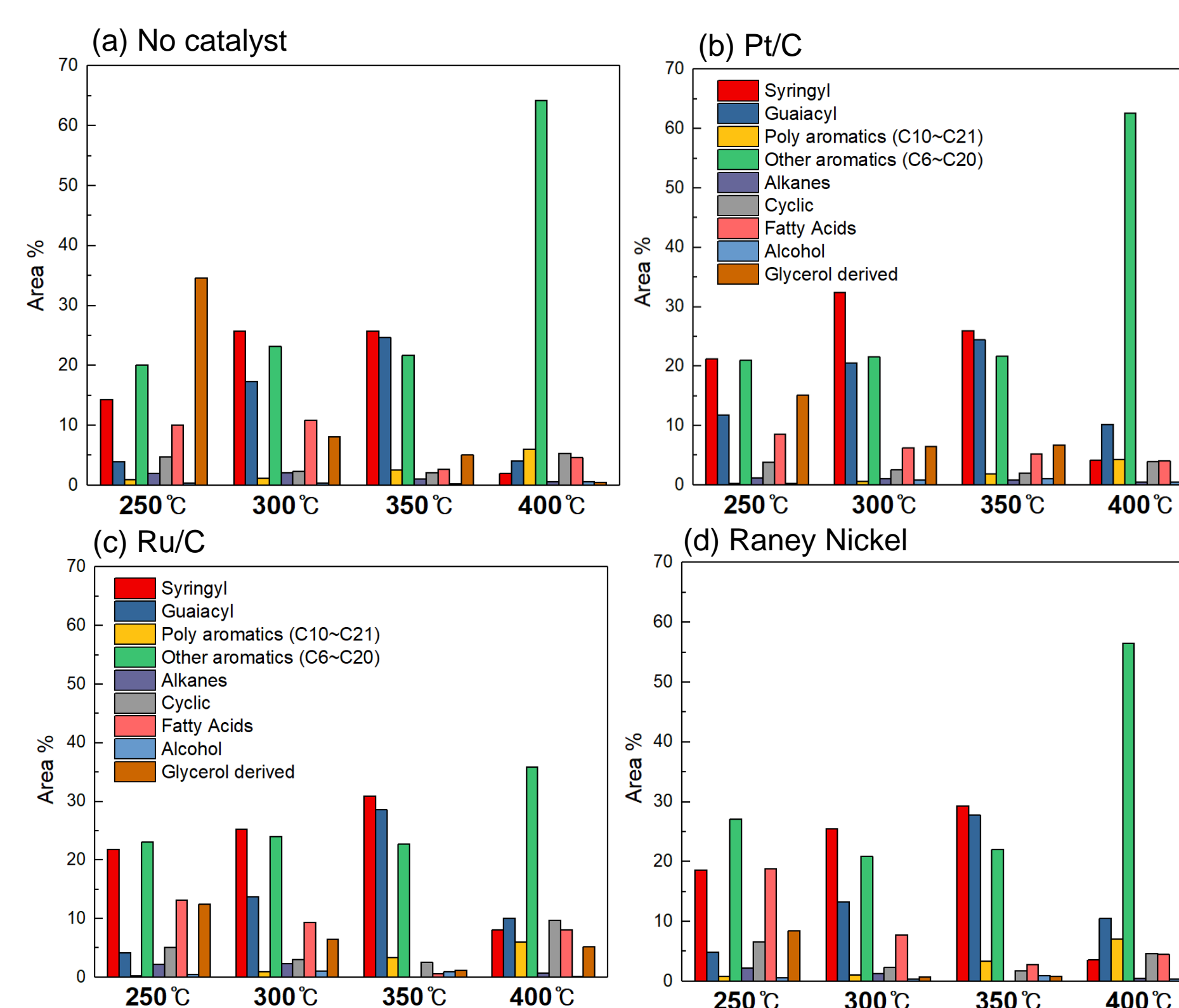


Gas composition (area%)

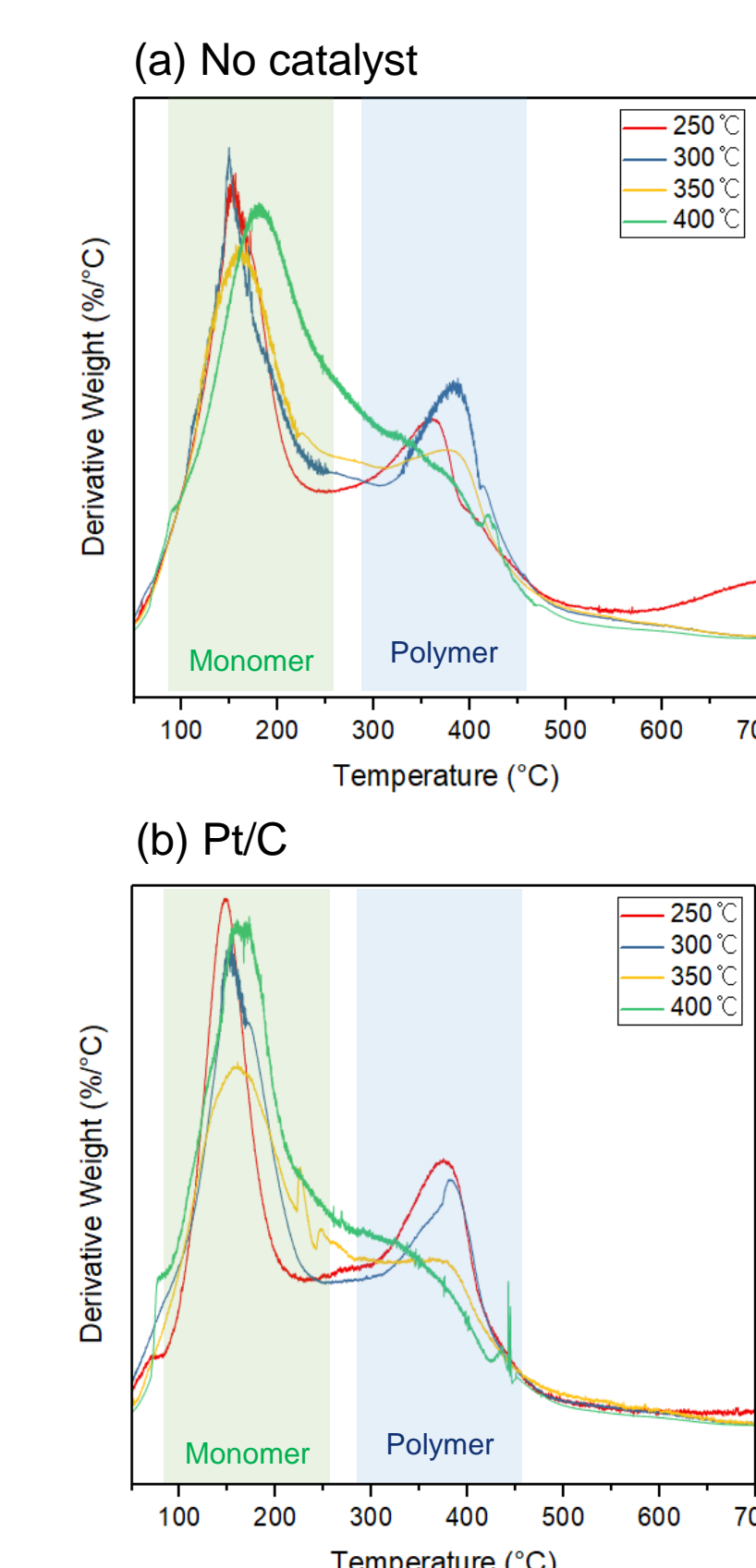
	H ₂	N ₂ , O ₂	CH ₄	CO ₂
-	250°C	4.36	12.31	4.14
	300°C	4.40	7.16	11.69
	350°C	9.08	2.21	32.24
	400°C	0.25	0.69	5.07
Pt/C	250°C	18.35	6.52	10.21
	300°C	14.75	3.49	17.09
	350°C	31.45	2.34	23.73
	400°C	0.84	1.43	3.97
Ru/C	250°C	35.85	9.87	1.76
	300°C	37.86	5.94	7.91
	350°C	28.37	2.68	25.00
	400°C	0.49	1.09	5.25
Raney Ni	250°C	23.26	10.36	7.32
	300°C	28.64	5.96	9.76
	350°C	19.77	3.07	26.07
	400°C	0.33	0.82	5.16

Analysis

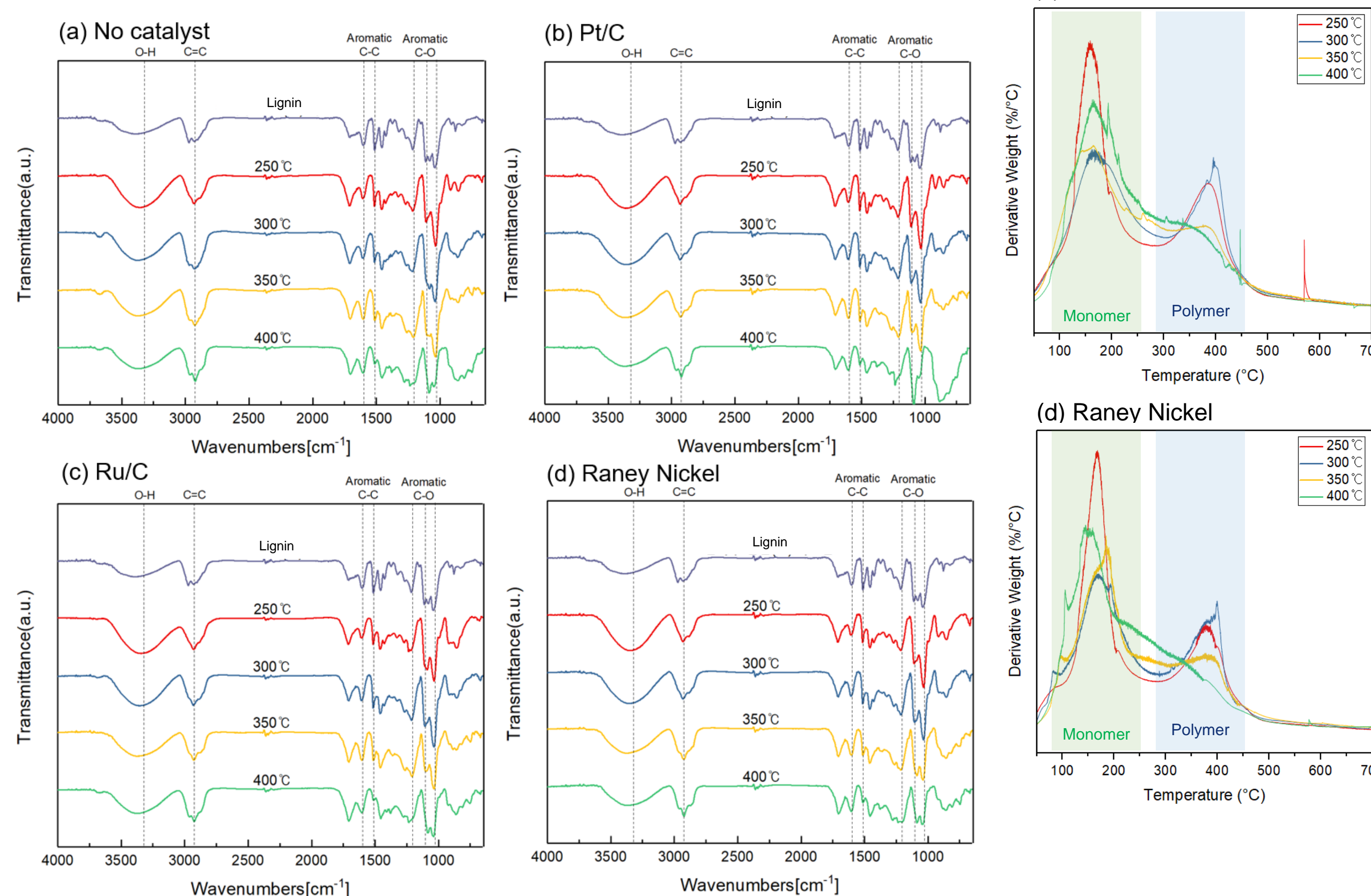
GC-MS Analysis of Bio-Oil



TGA Analysis of Bio-Oil



FT-IR Analysis of Bio-Oil



Conclusions

- The integrated process using glycerol increased bio-oil yield when catalysts were used compared to when no catalyst was used. The yield increased with temperature up to 350°C but decreased at 400°C.
- Glycerol aqueous phase reforming was analyzed by GC, showing that gas amount increased with temperature, with hydrogen production being highest with Ru/C catalyst, followed by Pt/C and Raney Ni. At 300°C, Ru/C produced the most gas and hydrogen.
- GC-MS results showed lignin-derived monomers (syringol, guaiacol) in all samples, with syringyl and guaiacyl groups increasing up to 350°C and decreasing at 400°C, where other aromatics (phenol, catechol, cresol) increased.
- FT-IR analysis identified peaks for aliphatic C=C bonds (2930 cm⁻¹), aromatic C-C bonds (1590, 1520 cm⁻¹), and aromatic C-O bonds (1260, 1110, 1030 cm⁻¹).
- TGA analysis revealed two major weight loss peaks: one at 100-280°C due to monomers, and another at 280-500°C due to polymer decomposition. Increased temperature resulted in decreased polymer peaks, indicating more monomer production.