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Comparison of *In-Situ* and *Ex-Situ* Catalytic Pyrolysis

Introduction

Catalytic pyrolysis is a promising technology to produce olefins and aromatics including benzene, toluene, and xylene when using HZSM-5 catalyst. Generally, there are two approaches to catalytic pyrolysis: in-situ and ex-situ. For in-situ catalytic pyrolysis, catalyst is introduced in the pyrolysis zone. For ex-situ catalytic pyrolysis, biomass is separately pyrolyzed and the pyrolysis vapors passed through a catalysis reactor downstream of the pyrolysis reactor.

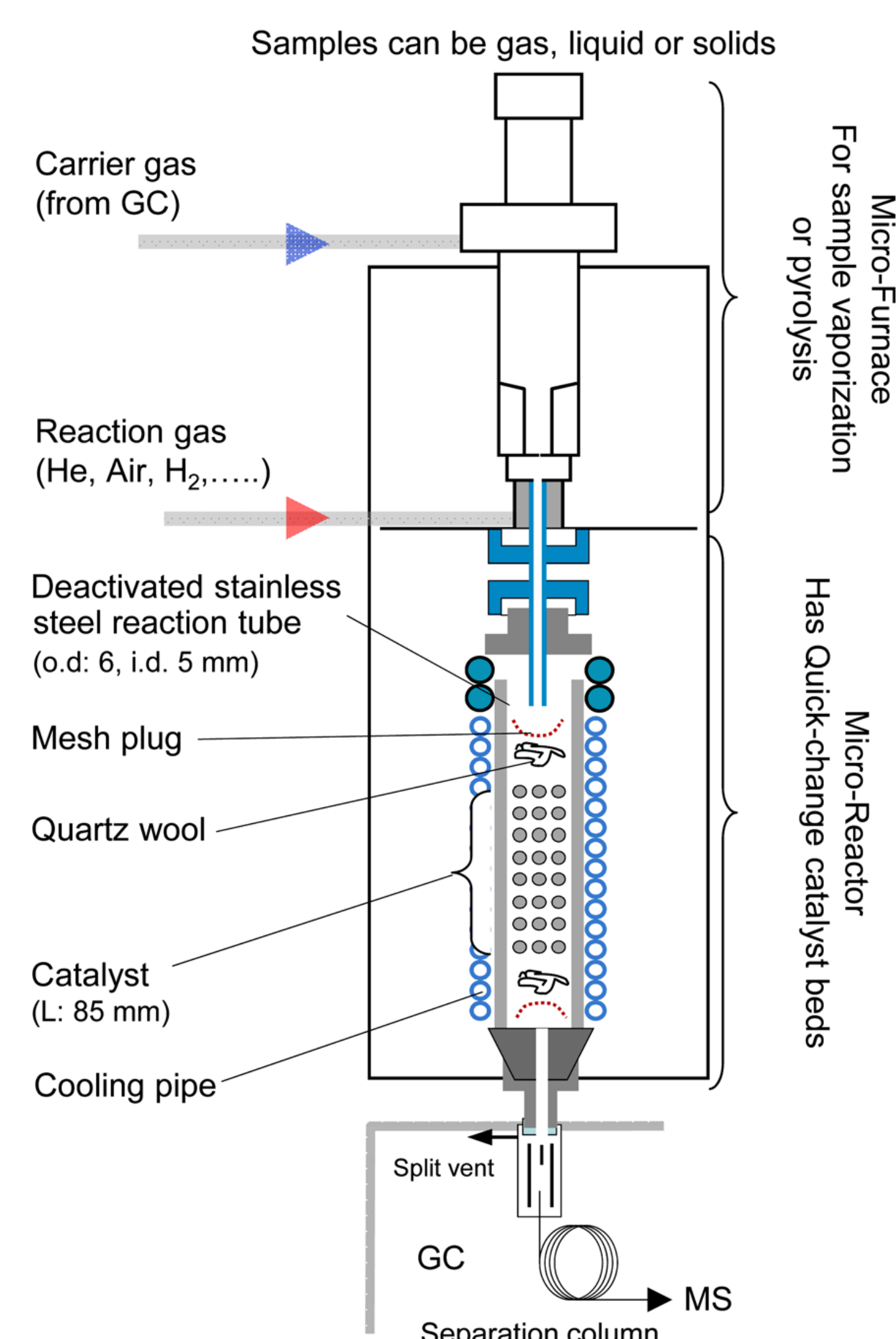
Objectives

- Compare in-situ and ex-situ catalytic pyrolysis of lignocellulosic biomass using H-ZSM5 zeolite
- For ex-situ catalytic pyrolysis, investigate the effects of catalyst loading and reaction temperature on yields

Methods

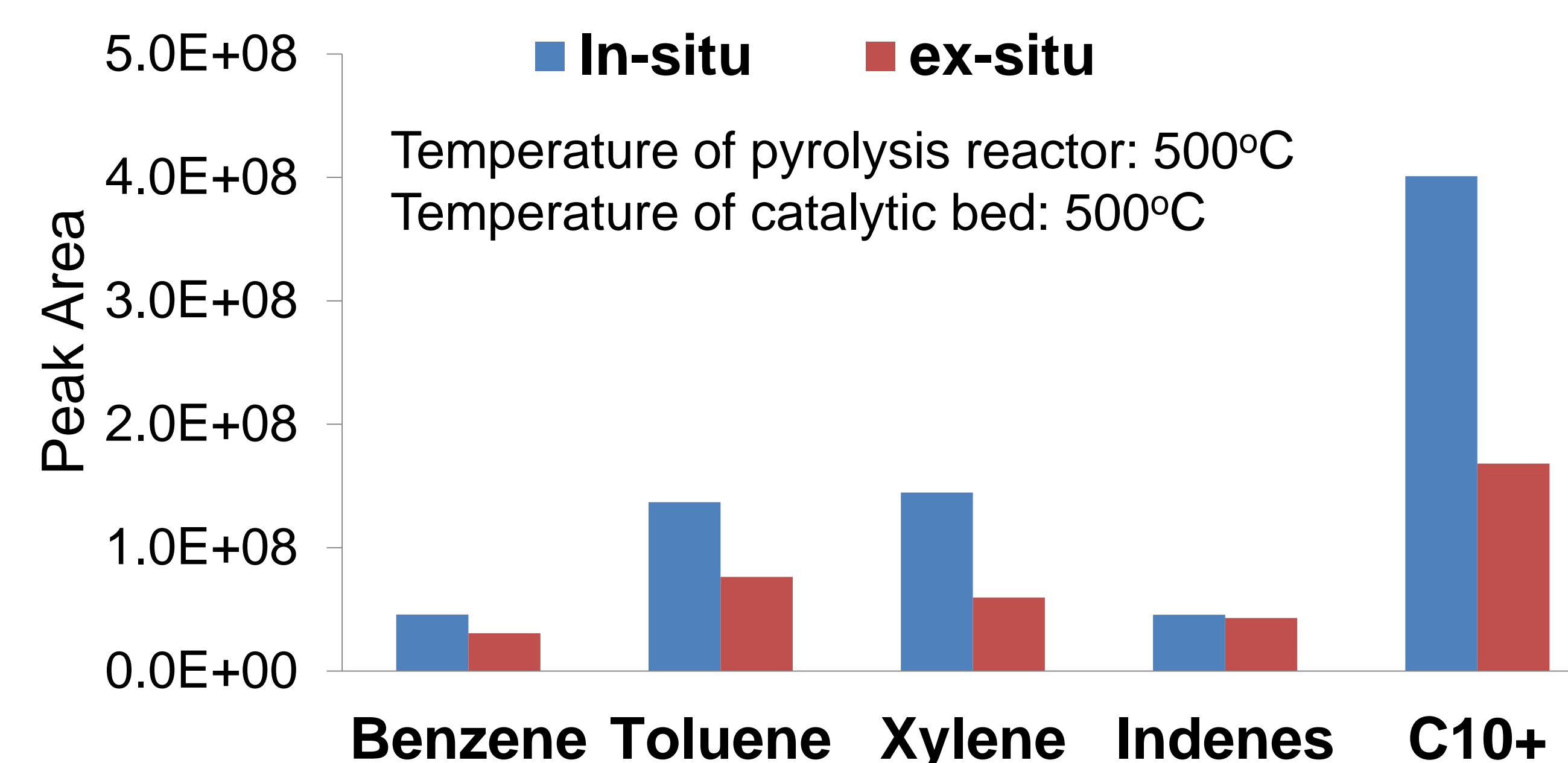
Pyrolysis experiment: Experiments were conducted with a Frontier 3050 Tandem Micro-Reactor System (see figure below), which consists of two furnaces connected in series. For ex-situ pyrolysis, biomass alone was pyrolyzed in the first furnace and the resulting pyrolysis vapors pass through a fixed bed of catalyst in the second furnace. For in-situ catalytic pyrolysis, a mixture of biomass and catalyst (1:20) was pyrolyzed in the first furnace while the second furnace was empty.

Materials: Hybrid poplar purchased from Wood Residual Solutions (USA) and ZSM5 catalyst (CBV2314) from Zeolyst (USA) was used in this study.

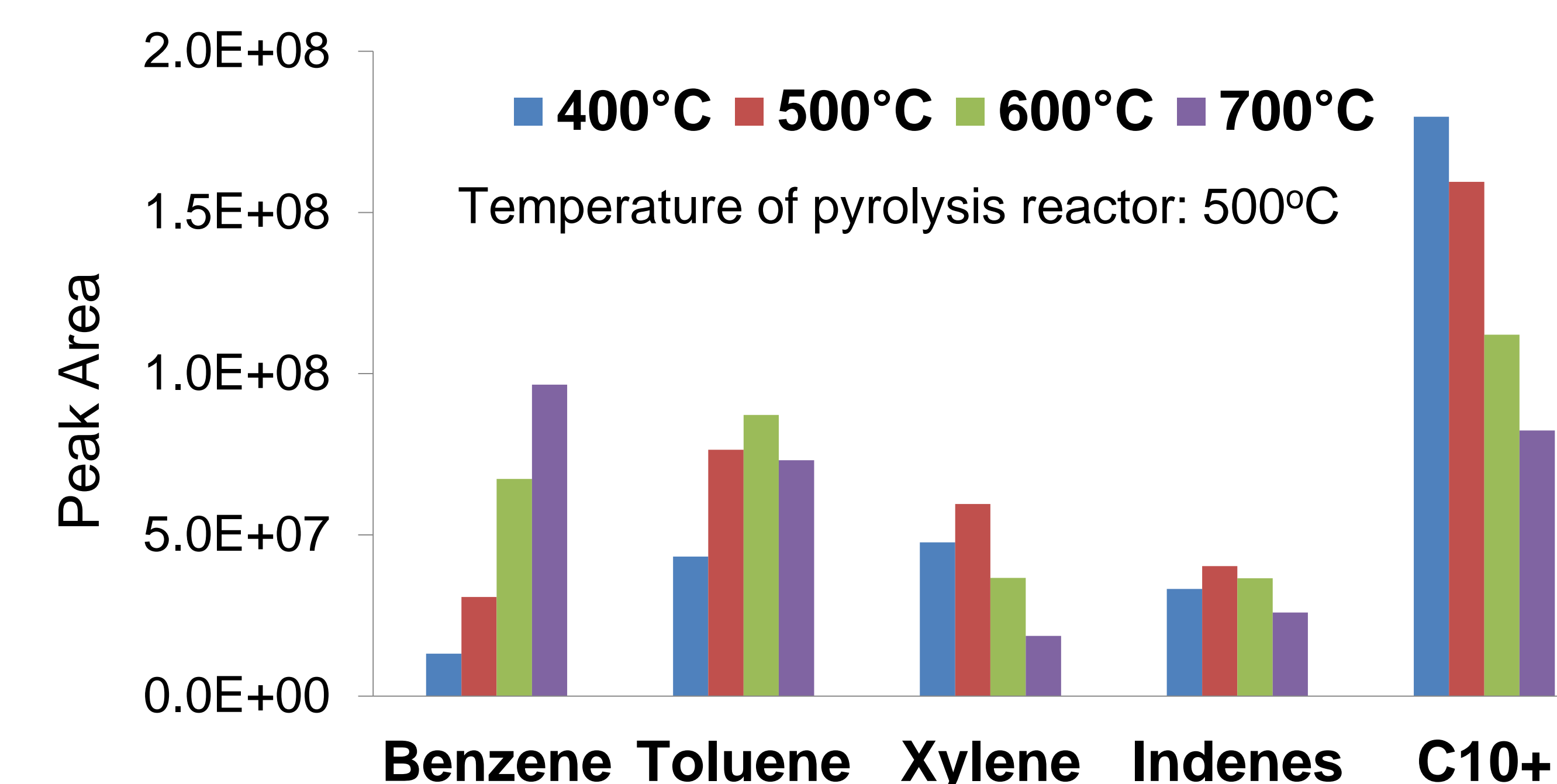


Results

Ex-situ catalytic pyrolysis produced less aromatics compared with in-situ

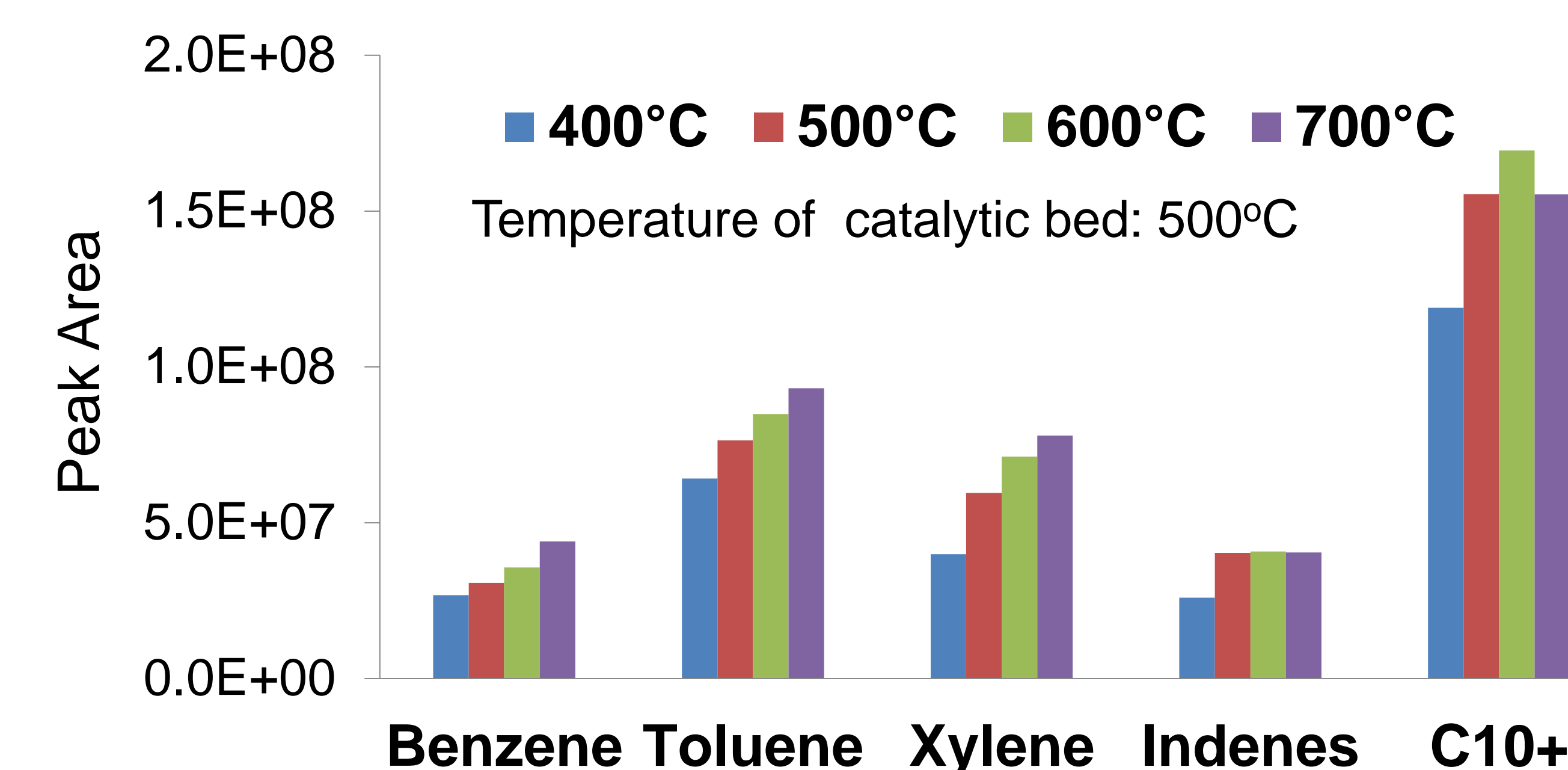


Ex-situ catalytic pyrolysis: Effect of catalytic bed temperature

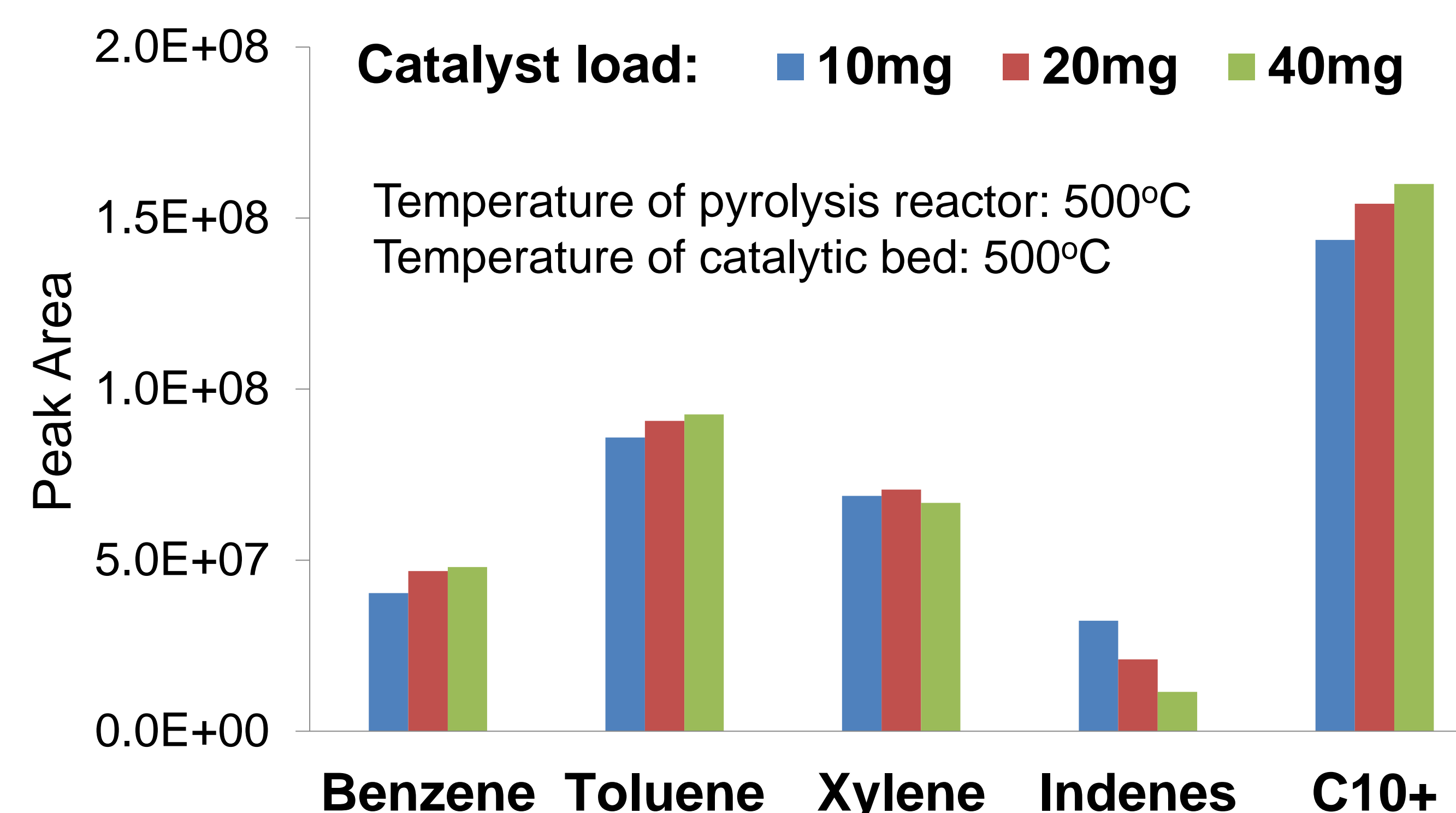


- Same reaction temperature and catalyst to biomass ratio (20:1) was used for the two methods (indenes include indene as well as alkyl-indenes; C10+ includes naphthalenes and higher polyaromatics).
- In-situ catalytic pyrolysis of hybrid poplar produced more aromatic hydrocarbons compared to ex-situ (twice as much for some aromatics)
- Ex-situ catalytic pyrolysis produced higher olefin yield than In-situ
- It is hypothesized that primary reactions of fast pyrolysis produce small enough molecules to diffuse into and react with the in-situ catalysts mixed with the pyrolyzing biomass.
- It is hypothesized that secondary condensation reactions downstream of the pyrolysis reactor produce aerosols that foul and coke the ex-situ catalysts, reducing aromatic yields compared to in-situ catalysts.

Ex-situ catalytic pyrolysis: Effect of pyrolysis temperature



Ex-situ catalytic pyrolysis: Effect of catalyst loading



- Higher temperatures favor the formation of small aromatics such as benzene and toluene.
- 500°C is an optimal temperature for catalytic conversion of pyrolysis vapor in terms of yield of valuable aromatics (BTX).
- Yield of aromatics increased with increasing pyrolysis temperature.

Future work:

- Compare in-situ and ex-situ catalytic pyrolysis of carbohydrates and lignin.
- Evaluate catalyst life.