

Pressure-Controlled Activity and Selectivity in Superbase-Catalyzed O-Vinylation of Menthol and Thymol with Acetylene

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Abstract

The pressure-dependent activity and selectivity of the potassium hydroxide–dimethyl sulfoxide (KOH–DMSO) superbases system were examined for acetylene O-vinylation of menthol and thymol at 130°C and 4–16 atm. Independent 250 mL parallel-reactor cells were charged with approximately 1.00 mol L⁻¹ substrate and 50 mol% KOH and stirred at 240 rpm. Gas chromatography with flame-ionization detection generated 0–120 min concentration profiles from three independent charges at each pressure. Comparison of integrated kinetic models by the Akaike information criterion selected apparent zero-order substrate consumption for all 14 substrate–pressure combinations. Between 4 and 12 atm, the apparent acetylene orders were 0.553 for menthol and 0.474 for thymol, demonstrating sublinear pressure responses of the catalytic system. Menthol vinyl-ether yield increased from 30.20% at 4 atm to 48.99% at 12 atm and subsequently approached a plateau. Thymol displayed a sharper activity–selectivity optimum at 14 atm, reaching 70.26% yield and 95.4% selectivity; at 16 atm, the yield decreased to 52.23% and secondary-product formation intensified. These substrate-specific responses show that increased acetylene pressure improves apparent catalytic activity only within a restricted operating window, beyond which secondary transformations compromise target-product formation.

1 Introduction

Direct nucleophilic addition of hydroxy compounds to acetylene is an atom-economical route to vinyl ethers, valuable intermediates and monomers. The synthetic scope of acetylene and calcium-carbide-derived acetylene has expanded markedly, while superbases systems remain particularly effective for O-vinylation [1–5]. In KOH–DMSO, alcohols and phenols form reactive anionic species whose addition to acetylene is strongly affected by solvation, ion pairing, and traces of water [1, 6].

Because acetylene vinylation is a gas–liquid process, the observed rate may combine intrinsic chemical kinetics with dissolution and interphase mass transfer. Acetylene solubility generally rises with pressure, whereas elevated temperature lowers physical solubility [7]. Consequently, pressure can accelerate reaction without producing a proportional rate increase, and apparent reaction orders obtained from pressure variation must not automatically be treated as elementary orders [8, 9]. Reaction-progress analysis and information-criterion-based model discrimination provide a defensible framework for separating empirical kinetic regimes [10, 11].

Earlier studies examined the mechanism of thymol vinylation in a superbasic medium [12] and mathematical modeling of thymol vinyl-ether synthesis [13]. Related work has further addressed stability-oriented modeling of naphthylacetic acid–poly(vinyl alcohol) systems [14] and biological-effectiveness assessment of functional chemical products [15]. Although the latter studies do not establish the elementary mechanism of acetylene O-vinylation, they support the broader relevance of coupling synthesis, stability, and end-use performance.

Mechanistic studies of acetylene hydrochlorination have shown that observed conversion and selectivity depend on the active center, the rate-determining addition step, and competing reaction pathways [16–

18]. Studies in Catalysis Letters likewise demonstrate that acetylene partial pressure, catalyst-site accessibility, carbonaceous deposits, and active-center stabilization can jointly govern apparent rates and product selectivity [19, 20]. Although these metal-catalyzed reactions differ from superbase-mediated O-vinylation, they provide a useful conceptual framework for distinguishing measured pressure responses from intrinsic elementary reaction orders. The present work therefore quantifies apparent zero-order rate constants over 4–16 atm, estimates apparent acetylene orders over 4–12 atm, and identifies the pressure-dependent activity–selectivity trade-off for menthol and thymol.

2 Experimental

2.1 Reaction System

Menthol (99%) or thymol (99%), dried DMSO (99%), KOH (85% assay), and acetylene (99.5%) were used. Each 145 mL charge contained 18.9418 g menthol or 18.2085 g thymol, 120 mL DMSO, and 3.9604 g KOH, corresponding to approximately 1.00 mol L⁻¹ substrate and 50 mol% KOH. In the GPXF-4×250 mL parallel reactor, stirring was 240 rpm, temperature was maintained at 130 ± 1 °C, and pressure at the set point within ± 0.2 atm.

2.2 Pressure Series and Analytical Measurements

Pressure was set to 4, 6, 8, 10, 12, 14, or 16 atm. Kinetic time began after stabilization of temperature and pressure; heat-up time was excluded. Samples were withdrawn automatically at 0, 15, 30, 45, 60, 90, and 120 min. Three independent charges were run at each pressure, yielding 147 concentration observations per substrate. Biphenyl was the internal standard. A Chromatec-Crystal 9000 GC–FID with a CR-5 column (30 m × 0.25 mm × 0.25 µm) was used. Calibration coefficients of determination were 0.9992 for substrate and 0.9988 for product; additional peaks were semi-quantified as the corresponding vinyl-ether equivalent.

2.3 Kinetic Modeling and Statistical Analysis

Integrated zero-, first-, and second-order models were compared by the Akaike information criterion on the original concentration scale [11]. For the selected zero-order model, $k_0 = \Sigma[t(C_0 - C)]/\Sigma t^2$ was calculated independently for each charge. Pressure dependence over 4–12 atm was described by $k_0 = KP^n$ and $\ln k_0 = \ln K + n \ln P$. The slope n and its 95% confidence interval were obtained by ordinary least-squares regression at the five pressure levels. The 14 and 16 atm points were excluded a priori from the power-law fit and examined as high-pressure diagnostics. Results are reported as mean ± standard deviation for three independent charges.

3 Results and Discussion

3.1 Pressure-Dependent Concentration Profiles

Increasing pressure from 4 to 12 atm accelerated substrate depletion and vinyl-ether accumulation for both substrates (Fig. 1). At 120 min, product concentration increased from 0.3020 ± 0.0018 to 0.4899 ± 0.0021 mol L⁻¹ for menthol and from 0.3097 ± 0.0054 to 0.4905 ± 0.0075 mol L⁻¹ for thymol. The thymol profile reached 0.7026 ± 0.0024 mol L⁻¹ at 14 atm but only 0.5223 ± 0.0077 mol L⁻¹ at 16 atm.

3.2 Apparent Zero-Order Kinetics

The zero-order model gave the lowest AIC for all 14 substrate–pressure combinations. Relative to zero order, Δ AIC values for first order were 2.7–12.6 for menthol and 2.9–11.4 for thymol; those for second order were 4.9–20.7 and 5.3–17.8, respectively. Pressure therefore changed k_0 without changing the apparent zero-order regime over 0–120 min. Table 1 and Fig. 2 summarize the resulting rate, yield, selectivity, byproduct, and resin responses.

Table 1
Principal results of the 120 min pressure series (mean $\pm$ SD, n = 3)

Substrate	P (atm)	k_0 (mol L ⁻¹ h ⁻¹)	Yield (%)	Selectivity (%)	Cbyproduct (mol L ⁻¹)	Resin (g)
Menthol	4	0.1145 $\pm$ 0.0005	30.20 $\pm$ 0.18	95.00	0.01589	0.01138
Thymol	4	0.1232 $\pm$ 0.0012	30.97 $\pm$ 0.48	90.00	0.02236	0.02122
Menthol	6	0.1427 $\pm$ 0.0002	35.00 $\pm$ 0.07	95.00	0.01842	0.01286
Thymol	6	0.1588 $\pm$ 0.0017	37.12 $\pm$ 0.55	90.60	0.02502	0.02375
Menthol	8	0.1877 $\pm$ 0.0005	46.36 $\pm$ 0.03	95.00	0.02440	0.01346
Thymol	8	0.1789 $\pm$ 0.0016	42.01 $\pm$ 0.59	91.20	0.02634	0.02500
Menthol	10	0.1964 $\pm$ 0.0006	48.56 $\pm$ 0.03	95.00	0.02556	0.01499
Thymol	10	0.1948 $\pm$ 0.0016	45.82 $\pm$ 0.63	91.20	0.02873	0.02727
Menthol	12	0.2022 $\pm$ 0.0003	48.99 $\pm$ 0.15	95.00	0.02578	0.01631
Thymol	12	0.2087 $\pm$ 0.0019	49.04 $\pm$ 0.65	91.20	0.03075	0.02919
Menthol	14	0.2234 $\pm$ 0.0006	48.15 $\pm$ 0.03	95.30	0.02375	0.02861
Thymol	14	0.2958 $\pm$ 0.0006	70.26 $\pm$ 0.13	95.40	0.03388	0.03224
Menthol	16	0.2084 $\pm$ 0.0006	49.89 $\pm$ 0.21	95.00	0.02626	0.02094
Thymol	16	0.2206 $\pm$ 0.0021	52.23 $\pm$ 0.67	90.20	0.03687	0.03500

Cbyproduct is expressed as the corresponding vinyl-ether equivalent.

3.3 Apparent Acetylene Pressure Order

Over 4–12 atm, $\ln k_0$ versus $\ln P$ gave $n_{\text{app}} = 0.553$ for menthol (95% confidence interval 0.312–0.793; $R^2 = 0.947$; $p = 0.0053$) and 0.474 for thymol (0.364–0.584; $R^2 = 0.984$; $p = 0.00084$) (Fig. 3). A threefold pressure increase raised k_0 by only 76.5% for menthol and 69.4% for thymol. The sub-unity slopes are

consistent with increased dissolved-acetylene availability combined with constraints imposed by interphase transfer, active basic species, or saturation; they are not evidence of fractional elementary stoichiometry [7–9].

3.4 High-Pressure Activity–Selectivity Trade-Off

For menthol, k_0 rose from 0.2022 to 0.2234 mol L⁻¹ h⁻¹ between 12 and 14 atm, but the 120 min yield decreased from 48.99 to 48.15% and resin increased from 0.01631 to 0.02861 g. At 16 atm, yield was 49.89%, only 0.91 percentage points above the 12 atm value. For thymol, 14 atm produced a distinct maximum: k_0 = 0.2958 mol L⁻¹ h⁻¹, 70.26% yield, and 95.4% selectivity. At 16 atm, k_0 and yield decreased by 25.4 and 25.7%, respectively, selectivity fell to 90.2%, and both byproduct and resin responses increased (Fig. 4). Thus, higher pressure did not monotonically improve target-product formation.

3.5 Substrate Dependence and Mechanistic Limitations

Menthol exhibited a comparatively smooth plateau, whereas thymol showed a narrow optimum at 14 atm. The difference is compatible with substrate-dependent ion pairing and solvation of alkoxide and phenolate species, although those microscopic states were not confirmed spectroscopically [6]. In related acetylene transformations, changes in accessible active sites, carbonaceous deposits, and catalyst stabilization have likewise altered kinetic responses and selectivity [19, 20], while isotope effects and stereochemistry have been used to distinguish limiting addition steps from faster downstream transformations [16–18]. These comparisons are methodological analogies rather than evidence that metal-catalyzed and superbase-catalyzed reactions share the same elementary mechanism. Because dissolved acetylene concentrations, volumetric mass-transfer coefficients, and independently verified active species were not measured, $n_{\text{acetylene}}$ is reported strictly as an apparent pressure-response exponent. Additional chromatographic peaks were quantified as vinyl-ether equivalents, and the polymer/resin measurement is operational and gravimetric.

4 Conclusions

Acetylene pressure significantly but sublinearly increased the apparent zero-order rate constant for menthol and thymol vinylation over 4–12 atm. The apparent acetylene orders were 0.553 and 0.474, respectively. Menthol yield approached a plateau above 12 atm, while resin formation became more prominent. Thymol had a narrow optimum at 14 atm, where the yield was 70.26% and selectivity 95.4%; both deteriorated at 16 atm. These results define a practical pressure window and demonstrate that higher acetylene pressure cannot be assumed to increase vinyl-ether yield monotonically.

Declarations

Ethics Approval

This article does not contain studies involving human participants or animals performed by any of the authors.

Competing Interests

The authors declare no conflict of interest.

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Author Contribution

M.I.S. conceived and designed the study, developed the methodology, performed kinetic modeling and statistical analysis, interpreted the results, and wrote the manuscript. S.E.N. contributed to the experimental design, supervised the research, and critically reviewed the manuscript. S.B.N. contributed to the experimental investigation, chromatographic analysis, and interpretation of the results. V.Z.A., A.S.A., and G.M.P. participated in the vinylation experiments, sample preparation, data collection, and analytical measurements. All authors reviewed and approved the final manuscript.

Data Availability

The time–concentration data and experimental metadata supporting the findings of this study are available from the corresponding author upon reasonable request.

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Figures

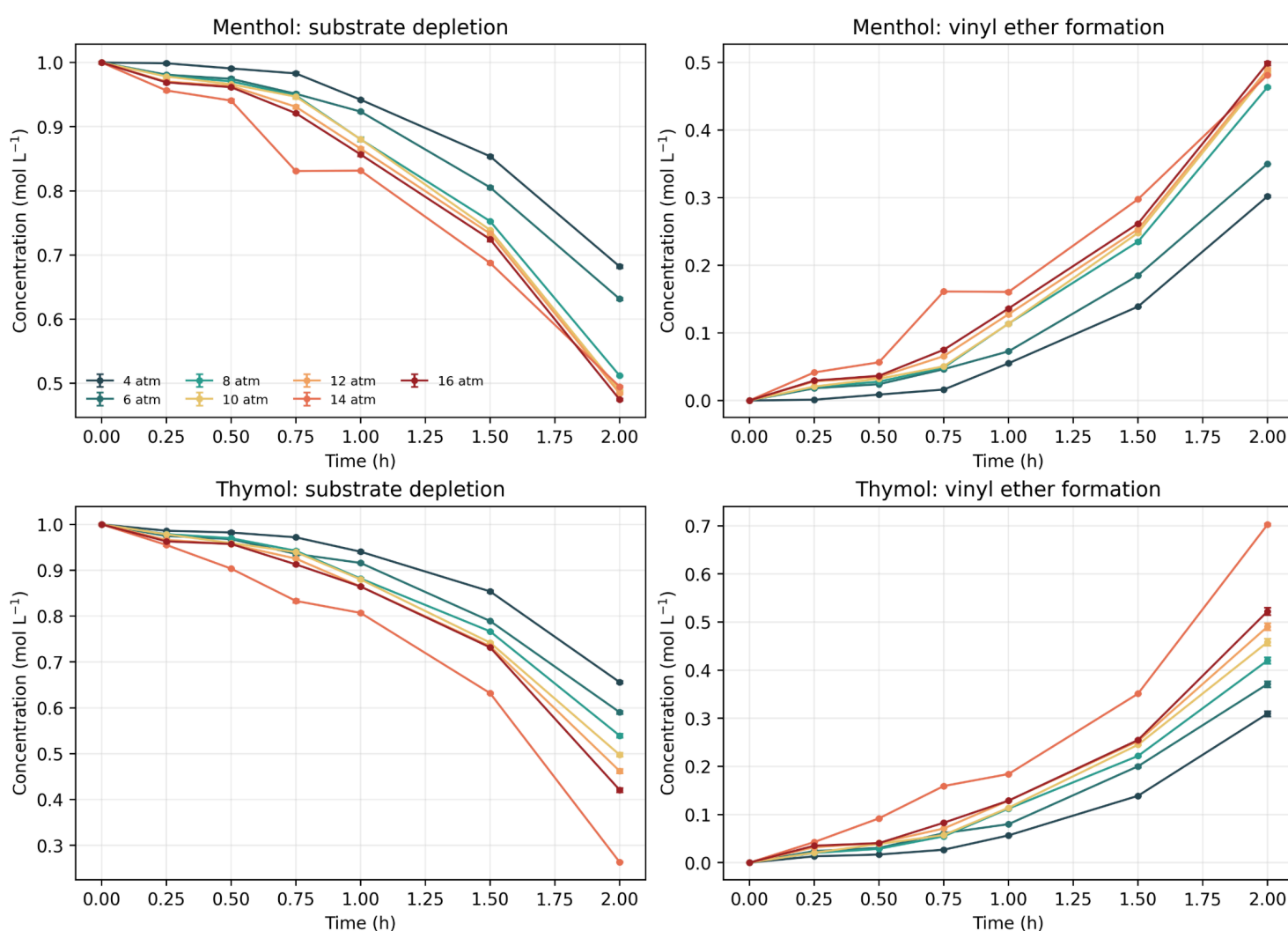


Figure 1

Pressure-dependent concentration profiles at 130°C, 50 mol% KOH, and 240 rpm (mean ± SD, n = 3)

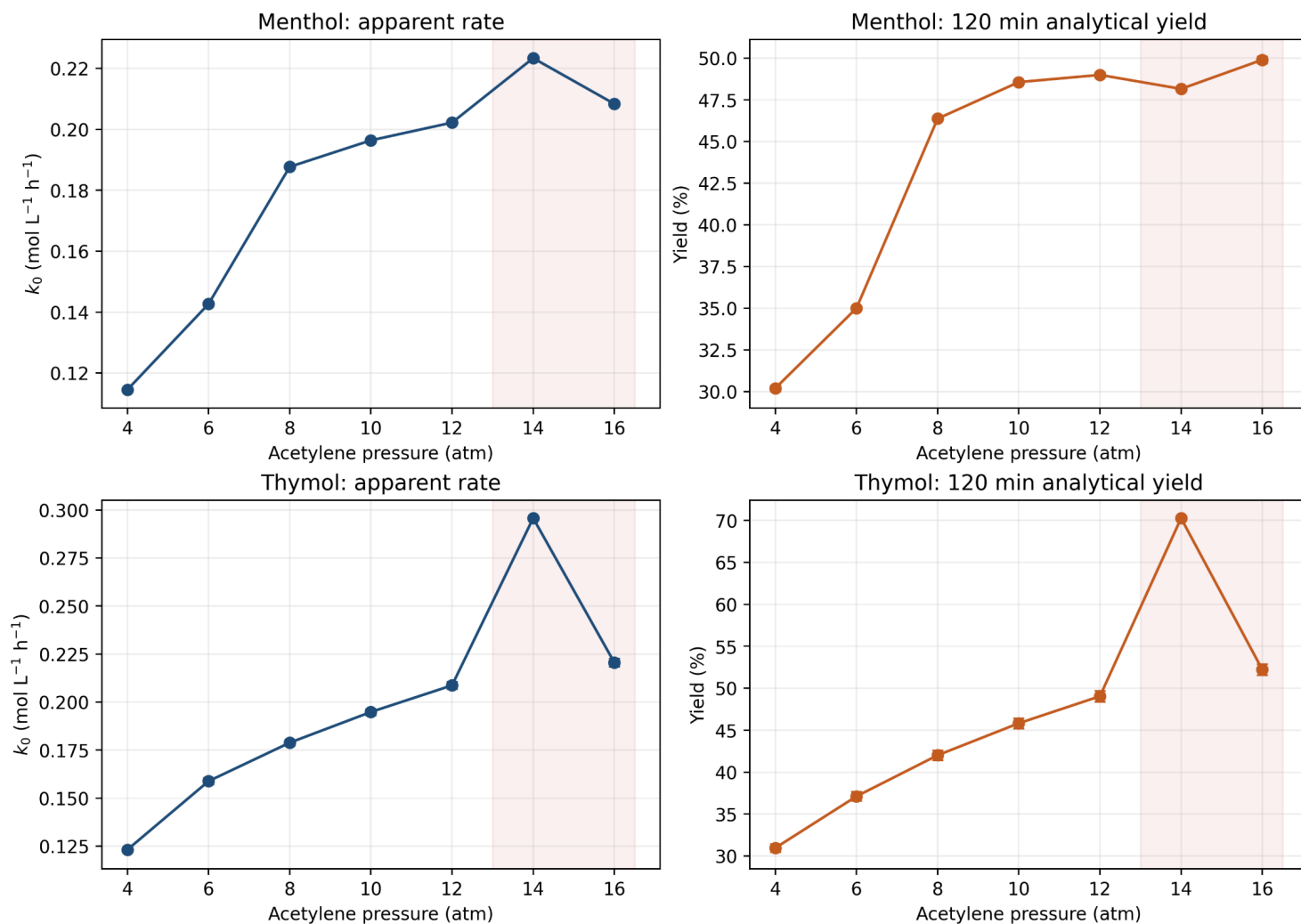


Figure 2

Effects of pressure on k_0 and 120 min analytical yield; the shaded range denotes the 14–16 atm high-pressure diagnostic region

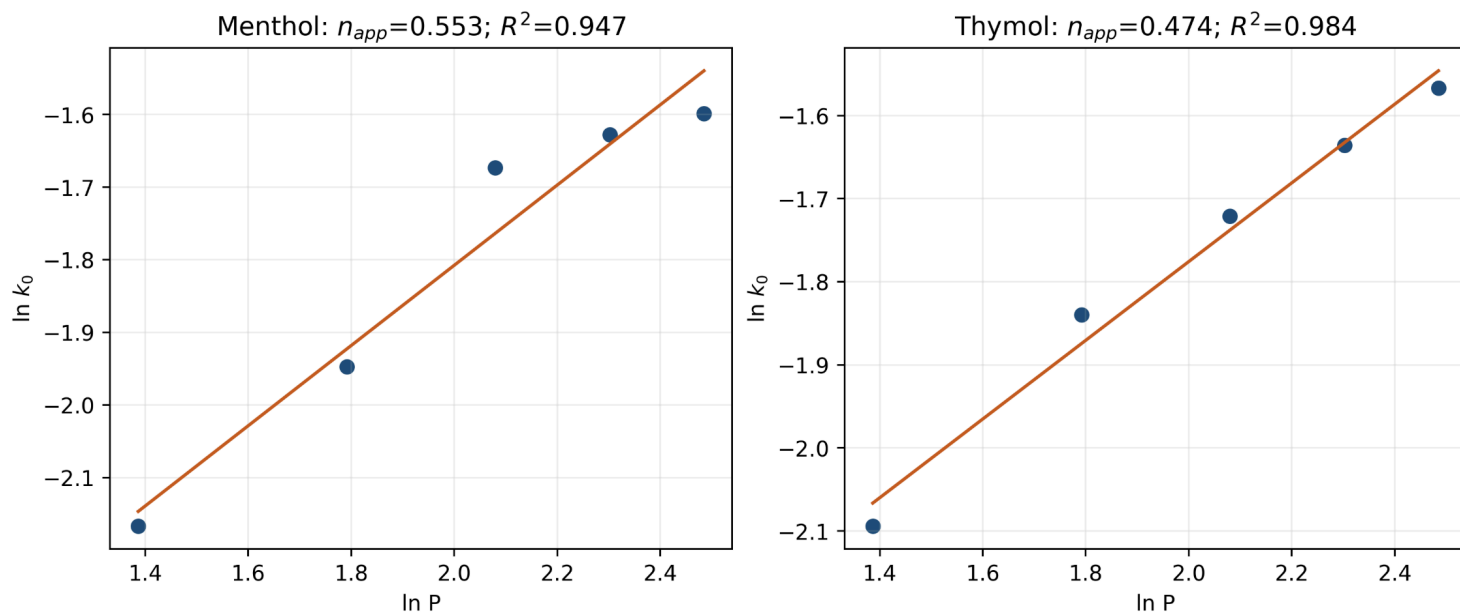


Figure 3

Power-law pressure model over 4–12 atm

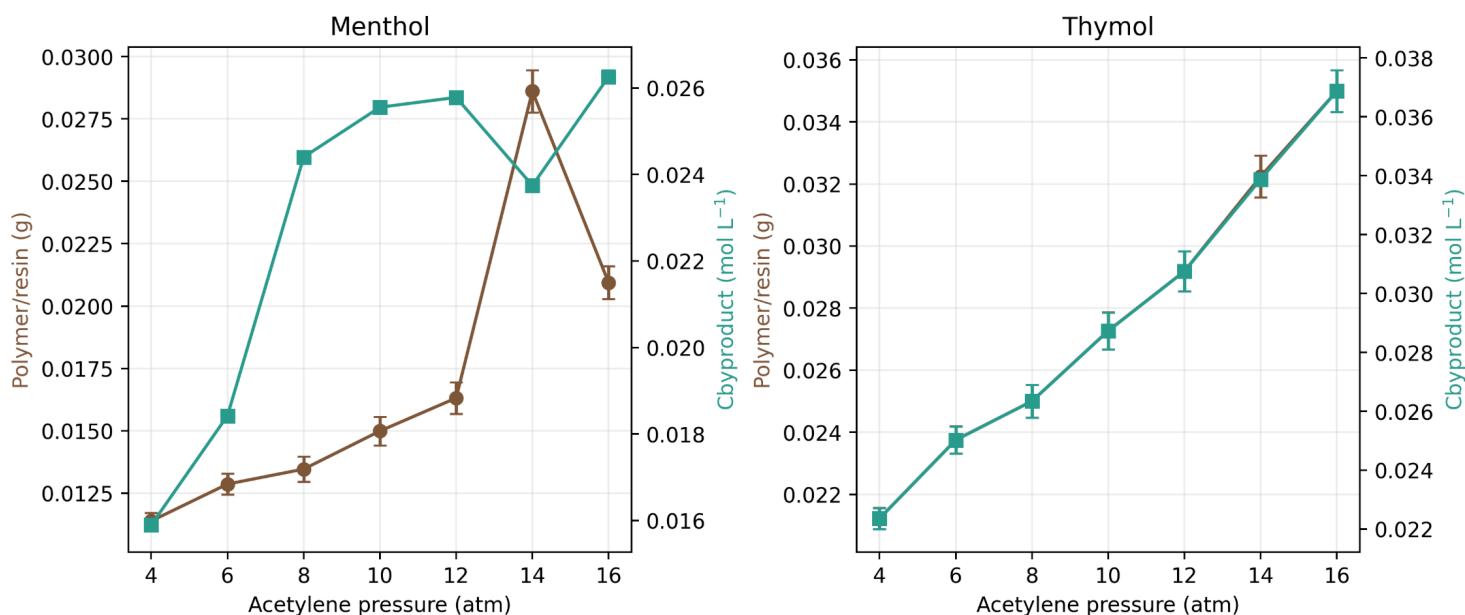


Figure 4

Pressure dependence of byproduct and polymer/resin responses at 120 min

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