

Long-Time Stability of Menthyl and Thymyl Vinyl Ethers in the Koh–Dmso–Acetylene System: Product Loss, Byproducts, and Polymer/Resin Formation

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Abstract

Long-time stability of menthyl and thymyl vinyl ethers formed by acetylene vinylation in KOH–DMSO superbase media was compared over 0–480 min at 130°C, 14 atm, 50 mol% KOH, and 240 rpm. Calibrated GC–FID Csub, Cproduct, and Cbyproduct values and dry polymer/resin mass were obtained from three independent reactor charges per time point. Product-formation and post-peak-loss regions were separated by a piecewise approach. Menthyl vinyl ether reached 0.93087 ± 0.00145 mol L⁻¹ and $93.09 \pm 0.09\%$ at 300 min; retention at 480 min was 96.48%, corresponding to 3.52% loss from the maximum. Thymyl vinyl ether peaked earlier, at 180 min, at 0.73000 ± 0.00209 mol L⁻¹ and $73.00 \pm 0.06\%$; retention at 480 min was 79.29%, a 20.71% loss. Apparent post-peak loss constants were 0.0099 h⁻¹ for menthol ($R^2=0.672$; $p = 0.180$) and 0.0620 h⁻¹ for thymol ($R^2=0.531$; $p = 0.100$), and were treated as descriptive parameters. At post-peak thymol points, product loss and polymer/resin showed perfect rank association (Spearman $\rho = 1.00$), whereas this association was not supported for menthol. Polymer/resin increased significantly with time by Kendall τ for both substrates: 0.778 ($p = 0.0024$) and 0.833 ($p = 0.00085$). Thymyl vinyl ether is therefore more sensitive to long-time secondary transformation and resinification. Approximate stopping times were 300 min for menthol and 180 min for thymol.

1. Introduction

Vinyl ethers combine high synthetic utility with pronounced chemical sensitivity arising from the electron-rich C = C–O unit. They undergo rapid cationic polymerization and can participate in radical addition, oxidation, hydrolysis, and rearrangement pathways, depending on impurities and reaction conditions [1–4, 13, 14]. This reactivity underpins their use in precision polymer synthesis, coatings, adhesives, and functional materials, but it also means that prolonged residence at elevated temperature may consume an initially formed target ether. Consequently, process optimization must address selectivity and residence time, not substrate conversion alone.

Direct addition of alcohols and phenols to acetylene remains an atom-economical route to vinyl ethers. Superbasic KOH–DMSO media enhance alkoxide nucleophilicity and have enabled the vinylation of alcohols, phenols, and naphthols; calcium carbide can also serve as an alternative acetylene source [5–8, 15]. Literature surveys note that secondary alcohols are less reactive than primary alcohols and that harsh basic/thermal conditions can promote tar formation and competing acetylene-derived reactions [5, 8]. The relevance of heteroatom addition to alkynes to the readership of Chemical Papers is demonstrated by Peixoto et al., who reported base-promoted hydrophenoxylation and hydrothiolation of activated alkynes to give vinyl-type O- and S-adducts [17], and by Ajiboye et al., who reviewed catalytic hydroalkoxylation across carbon-carbon multiple bonds [18]. These studies establish the journal-level context for alkyne hydrofunctionalization, but neither addresses the residence-time stability of vinyl ethers formed from unsubstituted acetylene. Previous technological and mathematical studies described the effects of temperature, pressure, KOH loading, and time on menthol/thymol yield [9–12].

However, a comparative long-time analysis combining target-product maxima, post-peak retention, chromatographic byproducts, and gravimetric polymer/resin response has not been reported.

This study identifies the menthyl and thymyl vinyl ether maxima over 0–480 min, describes post-peak product loss, evaluates dry polymer/resin and Cbyproduct responses, and defines an approximate stopping time for each substrate.

2. Materials and methods

2.1. Reaction conditions

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. Independent 250 mL cells of a GPXF-4×250 mL system were operated at 130 ± 1°C, 14.0 ± 0.2 atm, and 240 rpm.

2.2. Long-time series and analysis

Time zero was defined after internal temperature and pressure stabilization; heat-up was excluded. End points at 0, 60, 120, 180, 240, 300, 360, 420, and 480 min were evaluated. Each time point was treated as three independent reactor end-point charges (R1–R3). This distinction is essential: polymer/resin is not a cumulative mass measured in one reactor but the dry residue from a separate end-point charge, so its series need not be monotonic. Biphenyl was added to quenched samples as internal standard; Csub and Cproduct were determined with a Chromatec-Crystal 9000 GC–FID and CR-5 column. Additional peaks were semi-quantified as Cbyproduct in vinyl-ether equivalents. Polymer/resin is the gravimetric mass of dry residue—an operational indicator of polymerization/resinification, not structural identification.

2.3. Piecewise product-loss model

For each substrate, the maximum Cproduct (Cmax) and its time (tmax) were identified. At post-peak points, retention was 100Ct/Cmax and loss was expressed as ln(Cmax/Ct). A descriptive apparent loss constant was obtained from the slope of:

$$\ln(C_{\max}/C_t) = k_{\text{loss}}(t - t_{\max}).$$

The OLS result was sensitivity-checked with a Theil–Sen robust slope. Spearman ρ assessed post-peak product loss versus polymer/resin, and Kendall τ assessed time versus polymer/resin over the full series. $p < 0.05$ was used as a significance threshold; because of the small number of time points, k_{loss} was treated as a descriptive trend rather than an elementary constant.

3. Results and discussion

3.1. Long-time concentration profiles

Menthyl vinyl ether accumulated progressively to $C_{\text{max}} = 0.93087 \pm 0.00145 \text{ mol L}^{-1}$ at 300 min (Fig. 1). Between 360 and 480 min, concentration fluctuated modestly around the maximum but showed an overall declining tendency. Thymyl vinyl ether reached $C_{\text{max}} = 0.73000 \pm 0.00209 \text{ mol L}^{-1}$ earlier, at 180 min, followed by substantially greater loss. Thymol Cproduct minima at 300 and 420 min coincided with maxima in Cbyproduct and polymer/resin.

Table 1
Long-time series over 0–480 min (mean $\pm$ SD, n = 3).

Substrate	t (h)	Cproduct (mol L ⁻¹)	Cbyproduct (mol L ⁻¹)	Polymer/resin (g)	Yield (%)
Menthol	0	0.0000 $\pm$ 0.0000	0.0000	0.0000	0.00 $\pm$ 0.00
Thymol	0	0.0000 $\pm$ 0.0000	0.0000	0.0000	0.00 $\pm$ 0.00
Menthol	1	0.1605 $\pm$ 0.0018	0.0079	0.0176	16.05 $\pm$ 0.15
Thymol	1	0.1842 $\pm$ 0.0008	0.0089	0.0195	18.42 $\pm$ 0.10
Menthol	2	0.4815 $\pm$ 0.0008	0.0237	0.0286	48.15 $\pm$ 0.03
Thymol	2	0.7026 $\pm$ 0.0024	0.0339	0.0322	70.26 $\pm$ 0.13
Menthol	3	0.8781 $\pm$ 0.0026	0.0433	0.0244	87.81 $\pm$ 0.28
Thymol	3	0.7300 $\pm$ 0.0021	0.0352	0.0534	73.00 $\pm$ 0.06
Menthol	4	0.9019 $\pm$ 0.0020	0.0445	0.0309	90.19 $\pm$ 0.17
Thymol	4	0.6963 $\pm$ 0.0030	0.0336	0.0638	69.62 $\pm$ 0.17
Menthol	5	0.9309 $\pm$ 0.0015	0.0490	0.1584	93.09 $\pm$ 0.09
Thymol	5	0.5372 $\pm$ 0.0057	0.1872	0.2699	53.72 $\pm$ 0.46
Menthol	6	0.9163 $\pm$ 0.0024	0.0452	0.0419	91.63 $\pm$ 0.06
Thymol	6	0.6076 $\pm$ 0.0021	0.0293	0.0803	60.76 $\pm$ 0.16
Menthol	7	0.9244 $\pm$ 0.0024	0.0487	0.2334	92.44 $\pm$ 0.06
Thymol	7	0.4774 $\pm$ 0.0050	0.2584	0.3726	47.74 $\pm$ 0.41
Menthol	8	0.8981 $\pm$ 0.0013	0.0443	0.0512	89.81 $\pm$ 0.06
Thymol	8	0.5788 $\pm$ 0.0015	0.0279	0.0942	57.88 $\pm$ 0.06

3.2. Product maximum and stopping time

For menthol, analytical yield reached $93.09 \pm 0.09\%$ at 300 min, then was 91.63% at 360 min, 92.44% at 420 min, and 89.81% at 480 min (Fig. 2). Holding beyond 300 min therefore provided no additional target product. Thymol yield peaked at $73.00 \pm 0.06\%$ at 180 min, then was 69.63% at 240 min, 53.72% at 300 min, 47.74% at 420 min, and 57.88% at 480 min. Continuing beyond 180 min was therefore not only

inefficient but increased the risk of product loss. Conceptually, this need to stop the process near the target-product maximum agrees with the optimization principle reported by Hurst et al. in Chemical Papers: prolonged or more severe processing can decrease the desired-product yield while increasing solid residue and secondary products, so target yield and byproduct formation should be optimized jointly [19]. Although the underlying chemistry differs, the process-design implication is directly applicable to the present residence-time analysis.

3.3. Post-peak retention and apparent kloss

At 480 min, menthyl vinyl ether retained 96.48% of its maximum, corresponding to 3.52% post-peak loss. Thymyl vinyl ether retained 79.29%, a 20.71% loss. OLS kloss was 0.0099 h⁻¹ for menthol and 0.0620 h⁻¹ for thymol, a 6.3-fold greater thymol trend. However, fit p values were 0.180 and 0.100, and the Theil–Sen 95% slope intervals included zero. These constants are therefore descriptive comparative stability metrics, not definitive intrinsic kinetic parameters.

Table 2
Product maxima and post-peak stability parameters.

Substrate	tmax (h)	Ymax (%)	480 min retention (%)	Loss (%)	kloss (h ⁻¹)	R ²	p
Menthol	5	93.09 ± 0.09	96.48	3.52	0.0099	0.672	0.180
Thymol	3	73.00 ± 0.06	79.29	20.71	0.0620	0.531	0.100

3.4. Association with polymer/resin and byproducts

Across the full 0–480 min series, time and polymer/resin gave Kendall $\tau = 0.778$ ($p = 0.0024$) for menthol and $\tau = 0.833$ ($p = 0.00085$) for thymol. Despite endpoint fluctuations, resinification therefore tended to increase over prolonged time. At post-peak thymol points, ranks of $\ln(C_{\max}/C_t)$ and polymer/resin coincided (Spearman $\rho = 1.00$): the greatest product losses at 300 and 420 min coincided with the largest dry residues. For menthol, $\rho = -0.60$ ($p = 0.40$), so a direct association between product loss and individual dry-residue mass was not supported. This is consistent with greater post-peak menthyl vinyl ether stability and variability of endpoint gravimetry.

3.5. Mechanistic interpretation of the sequential process

The observations are consistent with a conditional $S \rightarrow P \rightarrow D/R$ sequence, where S is substrate, P is the target vinyl ether, D represents GC-observed byproducts, and R is polymeric/resinous residue. Product formation dominates initially; near tmax, the net rate approaches zero; thereafter, secondary consumption becomes relatively more important. Vinyl ethers are especially susceptible to cationic chain growth, while radical pathways are generally less favorable but can operate under appropriately initiating conditions [1–4, 14, 16]. In a hot KOH-DMSO-acetylene mixture, however, the residue may also

contain acetylene-derived oligomers and products of several secondary reactions [5, 8]. Because R was not characterized by SEC/GPC, FTIR, or NMR, the term polymer/resin is retained as an operational designation rather than evidence for a unique molecular mechanism.

3.6. Limitations

Nine time points and only 4–6 post-peak points limit precision of kloss. Because end-point charges were independent, lower dry-residue values may follow maxima at 300 and 420 min; they must not be interpreted as cumulative mass. Cbyproduct is a semi-quantitative aggregate in vinyl-ether equivalents, not a set of individually identified structures. GC–MS, SEC/GPC, FTIR, and $^1\text{H}/^{13}\text{C}$ NMR are required to characterize polymer/resin. Additional 270, 330, 390, and 450 min points would improve post-peak fit confidence.

4. Conclusions

At 130°C and 14 atm, menthyl vinyl ether reached 93.09% at 300 min and retained 96.48% of that maximum at 480 min; thymyl vinyl ether reached 73.00% at 180 min but retained only 79.29% at 480 min. Apparent kloss was 6.3-fold greater for thymol, although it was treated descriptively because of the small post-peak sample. Thymol product loss showed strong rank association with polymer/resin, and resinification increased significantly with time in both systems. Practically, the reaction should be stopped near 300 min for menthol and 180 min for thymol. Longer holding does not improve useful conversion and, particularly for thymol, promotes diversion of target product to byproducts and polymer/resin.

Declarations

Conflict of interest

The authors declares no conflict of interest.

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Author Contribution

M.I.S. conceptualized and designed the study, developed the methodology, supervised the research, curated the data, performed the statistical analysis and visualization, and wrote the original draft. M.I.S., S.E.N., S.B.N., V.Z.A., and G.M.P. jointly performed the experiments and contributed to data analysis and interpretation. M.I.S. reviewed and edited the manuscript. All authors read and approved the final manuscript.

Data Availability

The datasets generated and analyzed during the current study, including raw time–concentration data, replicate end-point measurements, calibration records, and statistical calculations, are available from the corresponding author on reasonable request.

References

1. Zhang J, Wu Y, Chen K, Zhang M, Gong L, Yang D, Li S, Guo W (2019) Characteristics and mechanism of vinyl ether cationic polymerization in aqueous media initiated by alcohol/B(C₆F₅)₃/Et₂O. *Polymers* 11:500. <https://doi.org/10.3390/polym11030500>
2. Sugihara S, Kawamoto Y, Maeda Y (2016) Direct radical polymerization of vinyl ethers: reversible addition-fragmentation chain transfer polymerization of hydroxy-functional vinyl ethers. *Macromolecules* 49:1563–1574. <https://doi.org/10.1021/acs.macromol.6b00145>
3. Teator AJ, Leibfarth FA (2019) Catalyst-controlled stereoselective cationic polymerization of vinyl ethers. *Science* 363:1439–1443. <https://doi.org/10.1126/science.aaw1703>
4. Namikoshi T, Hashimoto T, Kodaira T (2004) Living cationic polymerization of vinyl ethers with a tricyclodecane or tricyclodecene unit. *J Polym Sci Polym Chem* 42:3649–3653. <https://doi.org/10.1002/pola.20224>
5. Trofimov BA, Schmidt EY (2014) Reactions of acetylenes in superbasic media: recent advances. *Russ Chem Rev* 83:600–619. <https://doi.org/10.1070/RC2014v083n07ABEH004425>
6. Trofimov BA, Oparina LA, Kolyvanov NA, Vysotskaya OV, Gusarova NK (2015) Nucleophilic addition to acetylenes in superbasic catalytic systems: XVIII. Vinylation of phenols and naphthols with acetylene. *Russ J Org Chem* 51:188–194. <https://doi.org/10.1134/S1070428015020086>
7. Matake R, Adachi Y, Matsubara H (2016) Synthesis of vinyl ethers of alcohols using calcium carbide under superbasic catalytic conditions (KOH/DMSO). *Green Chem* 18:2614–2618. <https://doi.org/10.1039/C5GC02977E>
8. Ledovskaya MS, Voronin VV, Rodygin KS (2018) Methods for the synthesis of O-, S- and N-vinyl derivatives. *Russ Chem Rev* 87:167–191. <https://doi.org/10.1070/RCR4782>
9. Soliev MI, Okhundadaev AK, Nurmonov SE, Abidov I (2020) Reaction of vinylation of thymol with acetylene in a super-basic medium. *Universum Chem Biol* 10(76)

10. Soliev MI, Okhundadaev AK (2019) Mathematical modeling of the processes of synthesis of vinyl ether of thymols. *Int J Adv Res Sci Eng Technol* 6:10217–10222
11. Bektemirov A, Soliev M (2023) The study of the biological effectiveness of the AKARAGOLD 72% em.k. drug for solving problems of environmental protection. *E3S Web of Conferences*. 2023;417:02018. <https://doi.org/10.1051/e3sconf/202341702018>
12. Kakharova M, Soliev M, Ismailov N, Bakhronov K, Ochilova O, Abdullayeva S (2025) Modeling and analyzing naphthylacetic acid and polyvinyl alcohol technology for stability. *AIP Conference Proceedings*. 2025;3304:040010. <https://doi.org/10.1063/5.0269296>
13. Kirillov E, Rodygin K, Ananikov V (2020) Recent advances in applications of vinyl ether monomers for precise synthesis of custom-tailored polymers. *Eur Polym J* 136:109872. <https://doi.org/10.1016/j.eurpolymj.2020.109872>
14. Singha S, Pan S, Tallury SS (2024) Recent developments on cationic polymerization of vinyl ethers. *ACS Polym Au* 4:189–207. <https://doi.org/10.1021/acspolymersau.3c00055>
15. Rodygin KS, Ledovskaya MS, Voronin VV, Lotsman KA, Ananikov VP (2021) Calcium carbide: versatile synthetic applications, green methodology and sustainability. *Eur J Org Chem* 2021:43–52. <https://doi.org/10.1002/ejoc.202001098>
16. Miyamoto M, Sawamoto M, Higashimura T (1984) Living polymerization of isobutyl vinyl ether with hydrogen iodide/iodine initiating system. *Macromolecules* 17:265–268. <https://doi.org/10.1021/ma00133a001>
17. Peixoto MLB, Zandoná G, Silva MAM, Baig SA, Silva CHL, Silveira MV et al (2026) Valorization of water extract of banana peel ash: eco-friendly hydrophenoxylation and hydrothiolation of dialkyl acetylenedicarboxylates. *Chem Pap*. <https://doi.org/10.1007/s11696-026-04909-z>
18. Ajiboye TO, Ajala OJ, Adeyemi JO, Dhibar S (2024) Indium(III) complexes: application as organic catalyst, precursor for chalcogenides nanoparticles and starting materials in the industry. *Chem Pap* 78:4605–4622. <https://doi.org/10.1007/s11696-024-03411-8>
19. Hurst G, Brangeli I, Peeters M, Tedesco S (2020) Solid residue and by-product yields from acid-catalysed conversion of poplar wood to levulinic acid. *Chem Pap* 74:1647–1661. <https://doi.org/10.1007/s11696-019-01013-3>

Figures

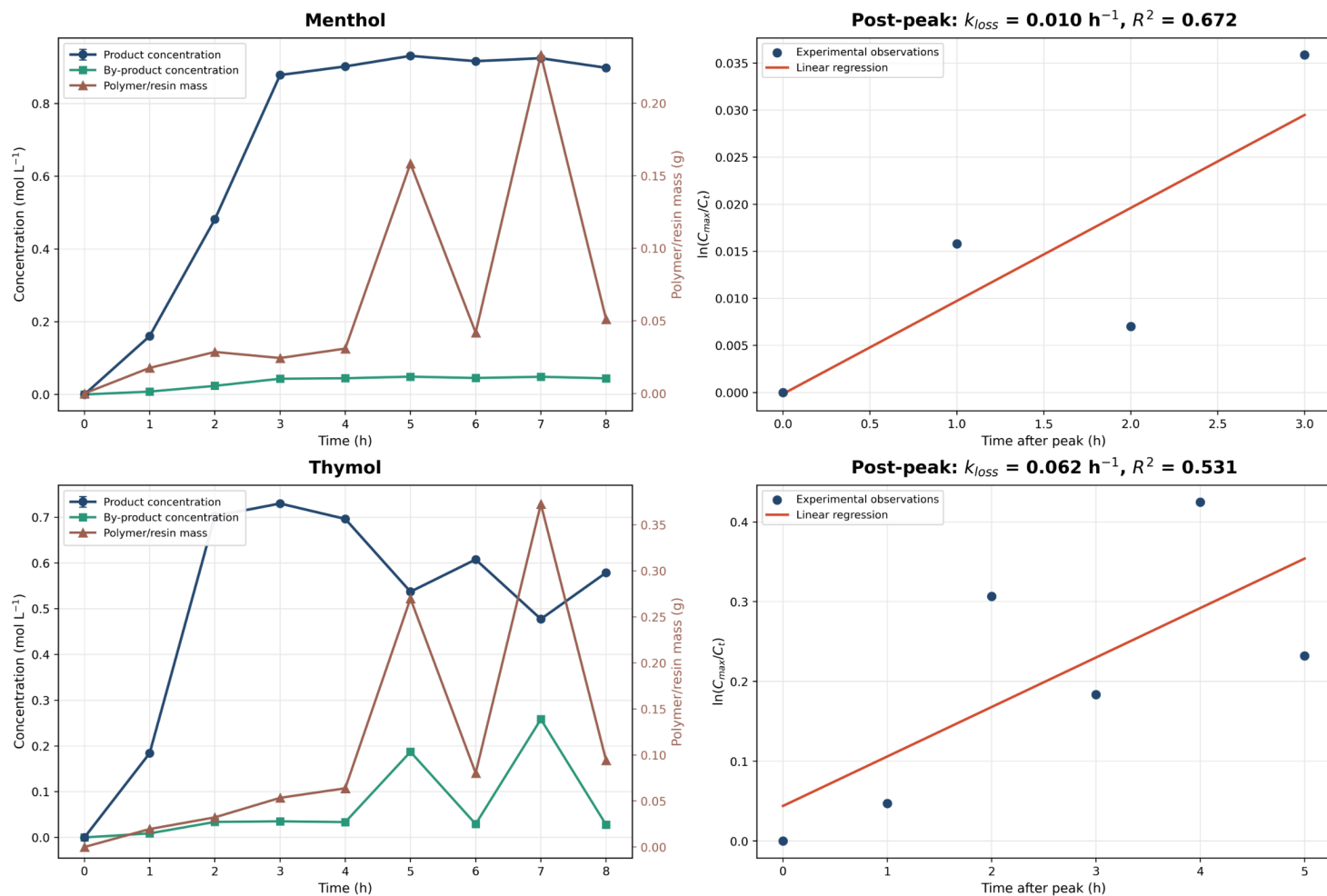


Figure 1

Long-time $C_{product}$, $C_{byproduct}$, and polymer/resin profiles and post-peak loss fits (mean $\pm$ SD, $n=3$).

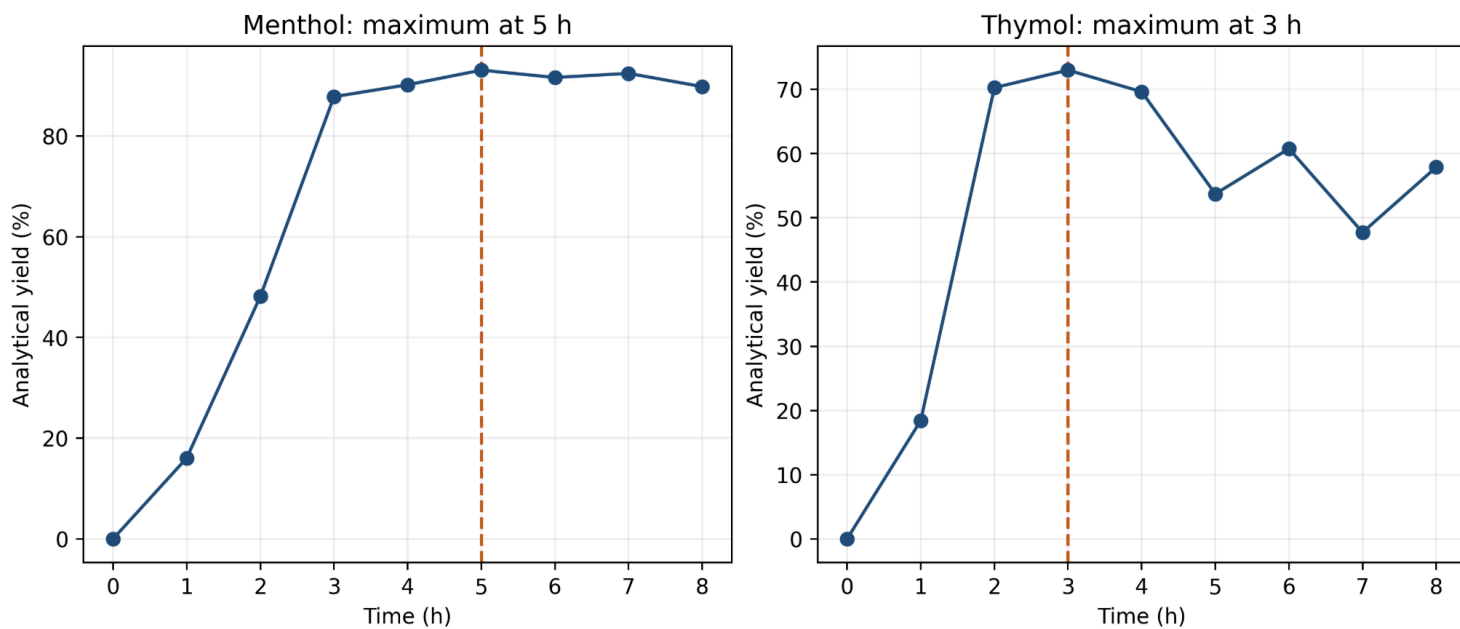


Figure 2

Analytical yield–time profiles and observed maxima.

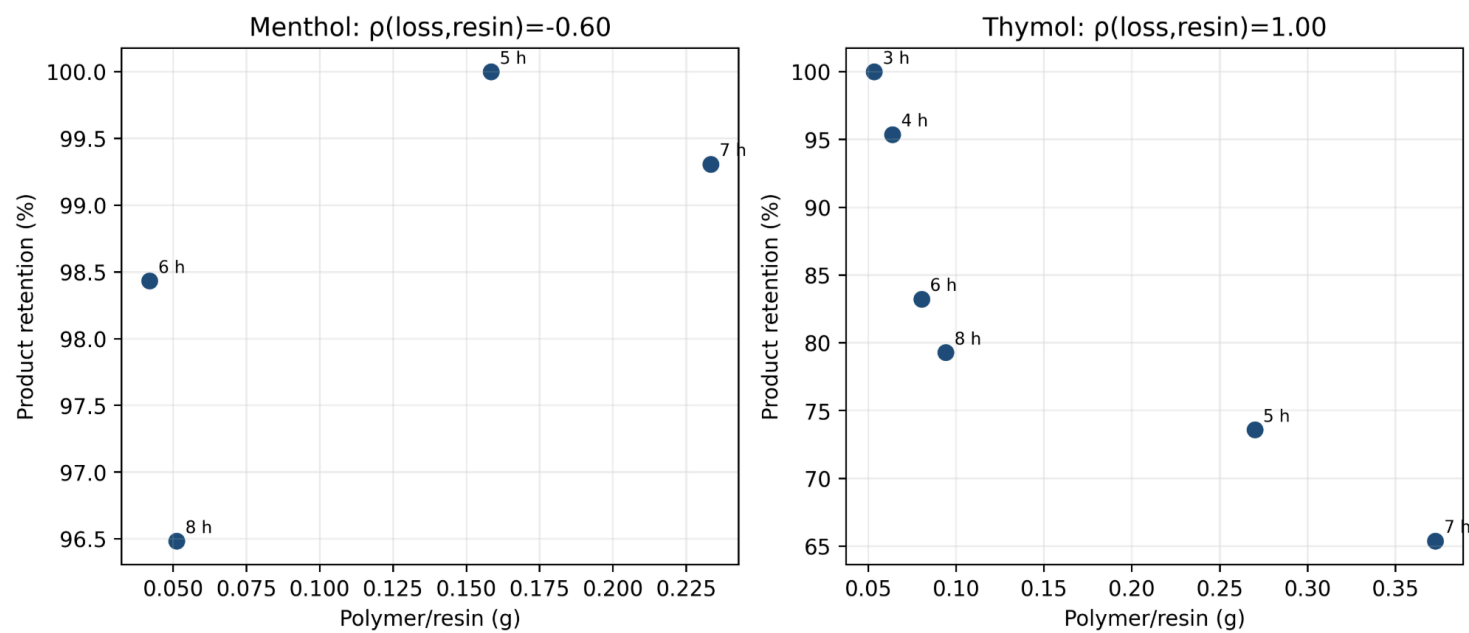


Figure 3

End-point relationship between post-peak product retention and polymer/resin.