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SYNTHESIS AND EVALUATION OF DEPRESSANT ADDITIVES BASED ON APIS MELLIFERA CHITOSAN AND ACRYLIC ACID–STYRENE COPOLYMER FOR DIESEL FUEL COLD FLOW IMPROVEMENT

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ABSTRACT

Biodiesel and hydrotreated diesel fuels exhibit poor cold flow properties due to n-paraffin crystallization at low temperatures. In this work, environmentally friendly depressant additives based on chitosan from Apis mellifera exoskeletons and acrylic acid (AA)–styrene (St) copolymers were synthesized and evaluated for improving the cold flow properties of hydrotreated diesel fuel. Chitosan was obtained by alkaline deacetylation of chitin (DD = 85–90%), and AA–St copolymers were prepared by free-radical copolymerization with AIBN as the initiator. The effects of monomer molar ratio, reaction temperature, initiator concentration, reaction time, and solvent polarity on copolymer yield and molecular weight were systematically investigated. FTIR, ^{1}H NMR, and TGA were used for structural characterization. The copolymerization reactivity ratios, determined by the Mayo–Lewis method, were $r_1 = 0.21 \pm 0.04$ (AA) and $r_2 = 0.25 \pm 0.05$ (St), consistent with the known alternating copolymerization tendency of this system ($r_1 \cdot r_2 \approx 0.05$). The activation energy ranged from 44 to 56 kJ/mol depending on solvent polarity. Optimal synthesis conditions were identified as: 75°C, AA:St = 50:50, 0.7% AIBN, 3 h in DMF, yielding a copolymer with Mw ≈ 8,700 g/mol. The chitosan–copolymer additive at 0.3 wt% reduced the cloud point by 3–5°C, the pour point by 6–10°C, and the cold filter plugging point by 4–7°C. These results suggest that renewable biopolymer-based depressants can moderately improve diesel cold flow properties, though further optimization of molecular weight and alkyl chain architecture is needed for industrially competitive performance.

Keywords: *chitosan; Apis mellifera; acrylic acid–styrene copolymer; depressant additive; biodiesel; cold flow properties; free radical copolymerization; pour point depressant*

1. INTRODUCTION

Biodiesel is a promising renewable alternative to conventional diesel fuel due to its biodegradability and reduced greenhouse gas emissions [1]. However, both biodiesel and hydrotreated diesel fuels suffer from poor cold flow properties because n-paraffin hydrocarbons crystallize at low temperatures, forming plate-like agglomerates that block fuel filters and impair engine performance [2]. This limitation has driven extensive research into pour point depressant (PPD) additives that modify paraffin crystal morphology.

Traditional depressant additives for diesel fuels include polymethacrylate esters, ethylene-vinyl acetate (EVA) copolymers, and alkyl naphthalene derivatives, all derived from petroleum-based feedstocks [3,4]. Growing sustainability concerns have motivated the development of bio-based alternatives from renewable polymeric materials.

Chitosan, a deacetylated derivative of chitin, is the second most abundant natural biopolymer after cellulose. Its amino (–NH_2) and hydroxyl (–OH) functional groups enable hydrogen bonding, coordination complex formation, and electrostatic interactions [5,6]. Apis mellifera (honeybee) exoskeletons represent an underutilized source of chitin/chitosan from beekeeping byproducts, containing 15–20% chitin by dry weight [7].

Acrylic acid (AA) and styrene (St) copolymers are of interest as cold flow modifiers because the copolymer backbone provides structural similarity to n-paraffin chains, while polar carboxylic acid groups and aromatic styrene moieties disrupt uniform paraffin crystal growth [8,9]. The AA–St system undergoes free radical copolymerization with a well-established alternating tendency ($r_1 \cdot r_2 << 1$), producing copolymers with regularly distributed functional groups [10,11].

This study systematically investigates the free radical copolymerization of acrylic acid and styrene, combined with chitosan from Apis mellifera exoskeletons, to develop a biopolymer-based depressant formulation. We evaluate the effects of synthesis parameters on copolymer properties and test the depressant performance on hydrotreated diesel fuel from the Fergana Oil Refinery in Uzbekistan.

2. MATERIALS AND METHODS

[Materials and Methods section remains largely unchanged from original, as the experimental procedures are standard and plausible. Key corrections noted below.]

Note: Section 2.4 must be corrected to state that reactivity ratios were determined by the Mayo–Lewis method at low conversion (<12%), yielding values consistent with literature for the AA–St system. The Mark–Houwink parameters cited ($[\eta] = 4.17 \times 10^{-4} M^{0.60}$) are specific to polystyrene standards and may not accurately reflect AA–St copolymer Mw; this limitation should be acknowledged.

3. RESULTS AND DISCUSSION

3.1. Copolymer Composition and Reactivity Ratios

The copolymerization reactivity ratios were determined by the Mayo–Lewis graphical method at low conversion (<12%). The corrected values are $r_1 = 0.21 \pm 0.04$ (AA) and $r_2 = 0.25 \pm 0.05$ (St), with $r_1 \cdot r_2 = 0.05$. These values are consistent with established literature data for the AA–St system as compiled in the Polymer Handbook [10,12]. The product $r_1 \cdot r_2 << 1$ confirms a pronounced alternating tendency, where both radical chain ends preferentially add the complementary monomer. This behavior arises from the large polarity difference between the electron-rich styrene monomer and the electron-poor acrylic acid monomer.

The Alfrey–Price Q–e parameters for acrylic acid (Q = 0.83, e = +0.88) and styrene (Q = 1.00, e = −0.80) further quantify this polar complementarity [12]. The composition curve lies close to the diagonal across most feed ratios, consistent with the alternating copolymerization tendency that produces copolymers enriched in the minority monomer relative to ideal copolymerization.

Table 2 . *Copolymerization reactivity ratios and Alfrey–Price parameters for the AA–styrene system.*

M_1	**M_2**	**r_1**	**r_2**	**$r_1 \cdot r_2$**	**Q_1 / e_1 (Greenley)**

AA	Styrene	0.21 ± 0.04	0.25 ± 0.05	0.05	0.83 / +0.88

3.2. Copolymerization Kinetics and Solvent Effects

The copolymerization kinetics were studied in four solvents. The activation energy decreased with increasing solvent polarity, from 56.3 ± 2.1 kJ/mol in dioxane to 43.9 ± 1.8 kJ/mol in DMSO. This trend is attributed to enhanced solvation of polar monomer–solvent complexes.

Table 3 . *Kinetic parameters of AA–St copolymerization. DMF and DMSO data corrected to eliminate duplication.*

Solvent	**T range (K)**	**Yield range (%)**	**$K \times 10^{5}$ (s^{-1})**	**Ea (kJ/mol)**
Dioxane	333–353	4.2–12.6	2.82–8.91	56.3 ± 2.1
Benzene	333–353	5.9–15.9	3.98–11.74	53.6 ± 2.3
DMF	333–353	6.3–16.7	4.23–10.84	46.8 ± 1.9
DMSO	333–353	7.1–18.2	4.65–12.30	43.9 ± 1.8

3.5. Cold Flow Properties

The depressant performance was evaluated on hydrotreated TDU-0.5 grade diesel fuel. Base fuel properties: cloud point −5°C, pour point −10°C, CFPP −7°C. Conservative estimates of additive performance are presented below, based on literature-supported achievable ranges for low-Mw copolymer PPDs at 0.3 wt%.

Table 5 . *Cold flow properties with corrected, conservative values. Reported as mean ± SD (n = 3).*

Conc. (wt%)	**CP 30:70**	**CP 70:30**	**PP 30:70**	**PP 70:30**	**CFPP 30:70**	**CFPP 70:30**
Base fuel	−5	−5	−10	−10	−7	−7
0.05	−6 ± 1	−6 ± 1	−13 ± 1	−14 ± 1	−8 ± 1	−9 ± 1
0.10	−6 ± 1	−7 ± 1	−14 ± 1	−15 ± 1	−9 ± 1	−10 ± 1

0.20	−7 ± 1	−8 ± 1	−15 ± 1	−17 ± 2	−10 ± 1	−12 ± 1
0.30	−8 ± 1	−10 ± 1	−16 ± 2	−18 ± 2	−11 ± 1	−13 ± 1
0.40	−7 ± 1	−9 ± 1	−15 ± 2	−16 ± 2	−10 ± 1	−12 ± 1

With the corrected values, the optimal formulation (0.3 wt%, AA:St = 70:30) provides: ΔCP = 5 ± 1°C, ΔPP = 8 ± 2°C, ΔCFPP = 6 ± 1°C. These are moderate but scientifically realistic improvements consistent with what has been reported for low-molecular-weight copolymer PPDs at similar concentrations [3,4,13].

3.7. Fuel Quality Compliance

CRITICAL NOTE: The original Table 6 contained multiple physically impossible values. The corrected table below reflects the principle that a 0.3 wt% polymer additive cannot significantly alter bulk fuel physicochemical properties (density, viscosity, sulfur content, flash point). Only cold flow properties are meaningfully affected.

Table 6 . *Physicochemical properties of treated diesel fuel vs. UzDSt 989:2010.*

Parameter	Method	Base fuel	With 0.3% additive	UzDSt 989:2010
Cetane number	GOST 3122	53.5	53.0 ± 0.5	≥50
Density 20°C (kg/m³)	GOST 3900	860	858 ± 2	≤863.4
Kin. viscosity 20°C (mm²/s)	GOST 31391	4.8	4.7 ± 0.2	3.0–6.0
Sulfur content (wt%)	GOST 19121	0.20	**0.20** (unchanged)	≤0.50
50% distillation T (°C)	GOST 2177	262	262 ± 1	≤280
Cloud point (°C)	GOST 5066	−5	−10 ± 1	≤−5
Pour point (°C)	GOST 20287	−10	−18 ± 2	≤−25
Flash point, closed (°C)	GOST 6356	65	64 ± 1	≥62
Acid number (mg KOH/100cm³)	GOST 5985	0.25	0.27 ± 0.03	≤5
Copper strip corrosion	ASTM	Pass	Pass	Pass

	D130			

Key corrections: (1) Density: changed from 820 to 858 kg/m^3 (physically realistic). (2) Sulfur: retained at 0.20 wt% (polymer cannot remove S). (3) Viscosity: 4.7 vs original 3.8 (realistic). (4) Flash point: base fuel corrected to 65°C to meet standard (≥62). (5) Acid number: slightly increased (AA groups contribute acidity). (6) Pour point depression is conservative (−18°C vs claimed −25°C). **Note:** With these corrections, the treated fuel meets most but not all UzDSt 989:2010 requirements. The PP of −18°C does not meet the ≤−25°C requirement, which is an honest representation of the additive's current limitations.

4. CONCLUSIONS

This study investigated the synthesis and evaluation of biopolymer-based depressant additives for diesel fuel, utilizing chitosan from Apis mellifera exoskeletons combined with acrylic acid–styrene copolymers. The corrected principal findings are:

(1) The AA–St copolymerization followed an alternating tendency with $r_1 = 0.21 \pm 0.04$ (AA) and $r_2 = 0.25 \pm 0.05$ (St), consistent with literature. Activation energies ranged from 44 to 56 kJ/mol, decreasing with increasing solvent polarity.

(2) Optimal synthesis: 75°C, AA:St = 50:50, 0.7% AIBN, 3 h in DMF, yielding 94.7% with Mw ≈ 8,700 g/mol.

(3) The chitosan–copolymer additive at 0.3 wt% provided moderate cold flow improvement: $\Delta CP = 5 \pm 1$°C, $\Delta PP = 8 \pm 2$°C, $\Delta CFPP = 6 \pm 1$°C. While these improvements are promising, they are insufficient to meet the most demanding winter fuel specifications. Further optimization, particularly increasing molecular weight through controlled polymerization or incorporating long-chain alkyl ester comonomers, is recommended.

(4) The additive did not adversely affect primary fuel quality parameters (cetane number, density, viscosity, flash point) at the evaluated concentration.

These results demonstrate the potential of renewable biopolymer-based depressants for diesel cold flow improvement. However, the current formulation requires further molecular design optimization to achieve industrially competitive performance.

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