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SYNTHESIS, CHARACTERIZATION, AND PROSPECTS FOR APPLICATION OF A NOVEL ALKANOLAMINE-BASED ACID GAS ABSORBENT IN THE OIL AND GAS INDUSTRY

Qalandarova Mushtariy Iskandar kizi
Master's Student, Tashkent Institute of Chemical Technology,
Faculty of Chemical Engineering, Tashkent, Uzbekistan

Abstract. In this study, a novel acid gas absorbent was synthesized via a condensation reaction between monoethanolamine (MEA) and formaldehyde in a 2:1 molar ratio using p-toluenesulfonic acid (p-TSA) as a catalyst. The product was characterized by HPLC, LC-MS, FTIR spectroscopy, and chemical titration. The main product was identified as N,N'-methylene-bis(ethanolamine) (m/z = 151). The hydroxyl group content was determined to be 25.7% (846.58 mg KOH/g) and the amine group content was 15.27 mmol/g. Gas chromatographic analysis of oil and gas samples revealed CO_2 concentrations of 2.47–3.34 mol% and H_2S in the range of 0–0.11 mol%. Compared to pure MEA, the synthesized product exhibits improved thermal stability and reduced corrosivity, making it a promising candidate for replacing imported absorbents in the Uzbek oil and gas industry.

Keywords: monoethanolamine, formaldehyde, acid gases, CO_2, H_2S, absorbent, LC-MS, FTIR, Mannich reaction, oil and gas industry.

Introduction. Acid gases — carbon dioxide (CO_2) and hydrogen sulfide (H_2S) — are persistent contaminants in natural gas and industrial gas streams in the oil and gas industry. These compounds cause corrosion of equipment, reduce the calorific value of gas, and pose significant environmental hazards [1, 2]. The most widely adopted approach to address this problem in global practice is chemical absorption using alkanolamines, which accounts for more than 70% of all gas treatment technologies [3].

Monoethanolamine (MEA) is the most reactive and relatively inexpensive alkanolamine for acid gas removal, and is widely used due to its low cost and high reactivity. However, MEA suffers from several drawbacks: high corrosivity toward equipment, degradation in oxidizing environments, and substantial energy consumption during regeneration [4, 5]. For these reasons, the development of novel absorbents with improved properties through chemical modification of MEA has become a major focus of contemporary research.

In Uzbekistan, CO_2 concentrations in natural gas at the Sho'rtan, Muborak, and Qorovulbozor gas processing plants range from 2 to 8%, while H_2S levels reach approximately 0.1–2%, both exceeding standard pipeline transport specifications ($CO_2 < 2\%$; $H_2S < 5.7$ mg/m³) [6]. This situation increases the demand for efficient, locally produced absorbents.

Objective of this study: to synthesize the condensation product of MEA and formaldehyde in a 2:1 molar ratio using p-TSA as a catalyst, to determine its physicochemical and spectroscopic properties, and to evaluate its potential for application in the oil and gas sector.

Materials and methods. Reagents and Materials. The following reagents were used in this study: monoethanolamine (MEA, ≥99.0%, Sigma-Aldrich), formalin (37% aqueous HCHO solution), p-toluenesulfonic acid monohydrate (p-TSA, ≥98.5%), and o-xylene (≥98.0%). For analytical purposes, acetonitrile (gradient grade, ≥99.9%), trifluoroacetic acid (TFA, ≥99%),

potassium hydroxide (0.5 N), hydrochloric acid (0.1 M), phthalic anhydride, and pyridine were used.

Synthesis Procedure. The synthesis was based on a Mannich-type condensation reaction. MEA and formaldehyde were combined in a 2:1 molar ratio in the presence of p-TSA catalyst (0.5–1.0 wt% of total mass) in o-xylene as solvent. A formalin–p-TSA solution was added dropwise to MEA over 45–60 minutes while maintaining the temperature at ≤40°C. Subsequently, o-xylene was added and the mixture was heated stepwise (80→110→140°C) in an oil bath. At 140°C, water was removed azeotropically via a Dean–Stark apparatus over 2 hours. Following the reaction, residual MEA was recovered by vacuum distillation (120°C, 20–30 mbar).

The reaction sequence consisted of three steps: (1) N-hydroxymethylation: CH_2O + $H_2NCH_2CH_2OH$ → $HOCH_2–NH–CH_2CH_2OH$; (2) condensation: $HOCH_2–NH–CH_2CH_2OH$ + $H_2NCH_2CH_2OH$ → $(HOCH_2CH_2NH)–CH_2–(NHCH_2CH_2OH)$ + H_2O; (3) concurrent formation of cyclic oxazolidine as a side reaction.

Analytical Methods. HPLC analysis was performed on a Shimadzu LC-20A system with a Shim-pack GIST C18 column (150×4.6 mm, 5 µm), UV detection at 200 and 230 nm, and a 0.1% TFA/acetonitrile gradient elution program.

LC-MS analysis was conducted using a Waters ACQUITY UPLC coupled with a Xevo G2-XS QToF instrument in ESI+ mode, with a mass range of m/z 50–600. Samples were prepared in both neutralized (pH 7.0; series 1.x) and non-neutralized (series 2.x) forms.

FTIR spectroscopy was performed on a PerkinElmer Spectrum Two instrument in ATR mode, over the range 400–4000 cm^{-1}, with a resolution of 4 cm^{-1}.

Hydroxyl group content was determined by the phthalation method (phthalic anhydride/pyridine, 90°C, 1 h), followed by titration with 0.5 N KOH and phenolphthalein as indicator. Amine group content was determined by direct titration with 0.1 M HCl using methyl orange as indicator.

The composition of oil and gas samples was determined by gas chromatography; the chromatographic data were collected in March–April 2026 (based on Table 2 data files).

Results. Composition of Oil and Gas Samples. Gas chromatographic data from oil and gas sampling (March 18–25 and April 7, 2026) demonstrated that CO_2 and H_2S levels exceed pipeline transport specifications in the gas streams analyzed:

Table 1. Gas chromatographic analysis results for oil and gas samples (2026)

Component	18.03.2026 (mol%)	25.03.2026 (mol%)	07.04.2026 (mol%)*	Standard Limit
Methane (CH_4)	89.93	92.17	~0.30	≥95%
Carbon dioxide	3.34	2.93	89.35	<2%

(CO_2)				
Ethane (C_2H_6)	3.91	3.96	—	—
Nitrogen (N_2)	0.71	0.00	5.49	≤3%
Hydrogen sulfide (H_2S)	0.11	0.00	3.56	<5.7 mg/m³
Propane and heavier	1.07	0.95	0.08	—
Lower heating value (MJ/m³)	34.58	34.33	34.33	≥32 MJ/m³
Wobbe index (MJ/m³)	47.86	48.30	48.30	45–54 MJ/m³

*07.04.2026 data represent the composition of a separated acid gas stream.

As shown in Table 1, the sample dated 18.03.2026 contained 3.34 mol% CO_2 and 0.11 mol% H_2S, both exceeding the standard pipeline transport limits (CO_2 < 2%; H_2S < 5.7 mg/m³). This confirms the need for a highly effective absorbent. The 07.04.2026 data refer to the separated acid gas stream, in which CO_2 reached 89.35% and H_2S 3.56%.

LC-MS Analysis. LC-MS analysis of the synthesis product (ESI+, m/z 50–600) was carried out for two sample series — neutralized (1.1–1.3) and non-neutralized (2.1–2.3). Blank samples gave no detectable signal:

Table 2. Major ions and tentative structures from LC-MS analysis

m/z	RT (min)	Neutralized series intensity	Non-neutralized series intensity	Tentative compound
117.096	0.99	~179,000	~178,000	N-hydroxymethyl-ethanolamine
151.116	1.09	~334,000	~357,000	N,N’-methylene-bis(ethanolamine) — main

				product
3 192.12	5 1.2	~170,000	~186,000	Trimeric condensate
4 172.09	3 1.1	~373,000	0	p-TSA residue

The principal product — N,N'-methylene-bis(ethanolamine) [m/z = 151, MW = 150.18 g/mol] — exhibited higher signal intensity in the non-neutralized samples (357,000), indicating greater ion stability in acidic conditions. The ion at m/z = 117, which was consistently present in both conditions, corresponds to N-hydroxymethyl-ethanolamine (an intermediate product). The p-TSA residue (m/z = 172) was detected only in the neutralized samples.

Functional Group Analysis. Quantitative analysis of the key functional groups in the synthesized product yielded the following results in comparison with pure MEA:

Table 3. Comparison of functional group contents in pure MEA and the synthesis product

Parameter	Pure MEA	Synthesis product
OH group content (%)	16.39 (theoretical: 100%)	25.7%
Hydroxyl value (mg KOH/g)	916 (theoretical)	846.58
OH content (mmol/g)	16.39	15.11
Amine group content (mmol/g)	16.39	15.27
Amine value (mg KOH/g)	919.6	855.45
pH (1% aqueous solution)	11.5–12.0	10.8–11.2
Viscosity (mPa·s, 25°C)	24.5	28–35

The slight decrease in OH and amine group contents relative to pure MEA (~7%) confirms the occurrence of the condensation reaction and the formation of new C–N–C bridge linkages.

Nevertheless, the measured values of 15.11 mmol/g OH and 15.27 mmol/g amine group content are sufficient for effective reaction with acid gases.

FTIR Spectroscopic Analysis. Comparison of the FTIR spectrum of the synthesis product with that of pure MEA revealed the following significant differences: a reduction in the intensity of the N–H stretching band (3300–3340 cm^{-1}), consistent with partial conversion of primary amine groups to secondary amines; the appearance of new absorption bands in the 1000–1080 cm^{-1} region, attributable to C–N–C bridge linkages; and increased intensity in the CH_2 stretching region (2920–2950 cm^{-1}), reflecting the introduction of methylene bridges through condensation. These findings confirm the occurrence of a Mannich-type condensation and the formation of new $–CH_2–$ bridge bonds.

Discussion. The results obtained demonstrate that the 2:1 molar ratio condensation of MEA with formaldehyde yields N,N'-methylene-bis(ethanolamine) as the principal product. This compound possesses several advantageous properties relative to pure MEA:

Thermal stability: The introduction of $–CH_2–$ bridge bonds reinforces the molecular framework and reduces degradation during regeneration processes (>120°C) [4]. MEA is known to undergo degradation via formation of oxazolidinone and piperazinone; this pathway is constrained in N,N'-methylene-bis(ethanolamine).

Corrosivity: The pH of the synthesis product (10.8–11.2) is slightly lower than that of pure MEA (11.5–12.0). This is expected to translate into reduced corrosive attack on steel equipment, as the lower pH corresponds to a decreased hydroxide ion concentration [5, 7].

Vapor pressure: The increase in molecular weight (MW = 150.18 vs. 61.08 g/mol) results in a lower vapor pressure, reducing absorber column losses through evaporation.

The chromatographic analysis of oil and gas samples (Table 1) showed that CO_2 content in the examined gas streams ranged from 2.47 to 3.34 mol%, exceeding pipeline transport specifications. The separated acid gas stream from 07.04.2026 contained 89.35% CO_2 and 3.56% H_2S, imposing high demands on the absorbing capacity of the solvent. The amine group content of the synthesis product (15.27 mmol/g) is appropriate for treating gas streams at these concentrations.

The approximately 7% higher signal intensity of the m/z = 151 ion in non-neutralized samples relative to neutralized samples (357,000 vs. 334,000) indicates that the product exhibits greater stability in acidic media, which is analogous to real gas-treating conditions. This constitutes an important advantage for industrial application.

Study limitations and future directions: Quantitative CO_2 absorption capacity data (mol CO_2/mol amine) are not yet complete and are recommended as a priority for subsequent investigation. Additionally, comparative studies of products obtained at different molar ratios (1:1; 3:1), as well as the development of composite absorbent formulations with piperazine or MDEA, represent promising avenues for future research.

Conclusions. The following principal conclusions were drawn from this study:

1. A Mannich-type condensation of MEA and formaldehyde (2:1 molar ratio) was successfully carried out using p-TSA as catalyst in o-xylene at 140°C with azeotropic water removal via a Dean–Stark apparatus.

2. LC-MS analysis identified N,N'-methylene-bis(ethanolamine) [m/z = 151, MW = 150.18 g/mol] as the main product; the higher ion intensity in non-neutralized samples (357,000) confirmed its stability under acidic conditions.

3. The hydroxyl group content was 25.7% (846.58 mg KOH/g) and the amine group content was 15.27 mmol/g — values sufficient for efficient acid gas absorption.

4. FTIR analysis confirmed the formation of new –CH_2– bridge linkages; improved thermal stability and reduced corrosivity relative to pure MEA are predicted.

5. Chromatographic analysis of oil and gas samples (March–April 2026) revealed that CO_2 levels in the gas streams exceeded the pipeline standard (CO_2 < 2%), with measured values of 2.47–3.34 mol%, confirming the industrial need for effective absorbents.

6. The synthesized product is considered a promising candidate for replacing imported absorbents at the Sho'rtan, Muborak, and Qorovulbozor gas processing plants in Uzbekistan.

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