Original Research Article

Evaluation of Red Onion Skin Extract as Inhibitor for Gum Formation in Gas Condensates

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ABSTRACT

In the upstream sector, gum in condensate causes significant erosion in value worth millions of dollars per annum and increases operational cost due to high injection concentration of conventional antioxidants. Phenolic compounds are commonly used at low concentrations in the downstream sector to inhibit gum formation in refined petroleum products. However, gum inhibition in condensates, in the upstream sector, requires high concentrations of phenolic antioxidant. Therefore, there is need for cheaper and more effective antioxidants for gas condensates. The present study investigates the use of red onion skin extract (ROSE) as a natural inhibitor for gum formation in condensate based on ASTM D381. Treatments with ethanolic extracts of red onion skin were carried out on seven gas condensate samples with gum formation tendency. At a dosage of 200ppm red onion skin extract caused a reduction of 17.4% to 99.6% in washed gum content of the condensate samples. The performance of ROSE was comparable to, and in some condensates better than, commercially available catechol. The result obtained using ROSE highlights the need to explore the commercial viability of this application in oil & gas upstream operations.

Keywords: [gum inhibition, gas condensate, red onion skin extract, antioxidant]

1. INTRODUCTION

Gum refers to the resinous, non-volatile, high molecular weight polymeric material formed in fuels in storage or when exposed to high temperature condition such as during combustion in engines [1]. Gum formation and inhibition in refined petroleum products such as gasoline, diesel and aviation fuel has been extensively studied as a result of its impact on product storability and engine performance but similar studies on gas condensates are scarce [2 - 6].

Condensate is a low-density high API gravity liquid that condenses from the gas phase when the temperature at a given pressure falls below the dew point. The term describes hydrocarbon fluids that may encompass a wide molecular weight range because the paraffin composition of condensates varies depending on the well and operation conditions under which they are produced. Because some condensates contain relatively high molecular weight alkanes which do not evaporate under the test conditions of ASTM D381, resulting in deposition of non-gum material, it has been proposed that washed gum content is a more appropriate quality parameter for gas condensates rather than unwashed gum content [7].

Gum formation is believed to be a free-radical chain polymerization process mediated by peroxy radicals [1, 3]. The presence of trace heavy metals such as iron, copper, cobalt and manganese increase the rate of gum formation because they facilitate the production of peroxides by catalyzing the decomposition of hydroperoxide [1]. Resins and asphaltenes although present in low concentration in condensates, increase the potential for gum formation in condensates due to their large polycondensed heteroaromatic structures. Gum content is an important quality parameter for gas condensates and a determinant of market value [7].

Antioxidants are natural or synthetic compounds that can at low doses inhibit oxidative damage (mediated by peroxy radicals) to other molecules [8]. They are usually phenolic compounds or substituted phenylenediamines. Phenolic antioxidants are important antioxidants in biological systems. Dietary phenolic compounds such as tocopherol, ascorbic acid and flavonoids are believed to be effective in prevention of several diseases related to oxidative stress [8, 9]. The antioxidant property of phenolics is due to their ability to react with peroxy radicals to form resonance-stabilized phenoxy radicals, essentially acting as radical scavengers. A number of phenolic compounds including catechol, resorcinol, hydroquinone and amino phenol have been evaluated as hydrogen peroxide scavengers [8].

Red onion (*Allium Cepa)* contains high concentration of quercetin, an essential phenolic antioxidant belonging to the flavonol sub-class of flavonoids [10, 11]. Onion is one of the vegetables with the highest quercetin content [12]. The skin of red onion is an agricultural waste [13]. Interestingly, red onion skin has been found to have much higher concentrations of quercetin than the flesh [14]. Red onion skin extract (ROSE) is a quercetin-rich natural material easily extractable from the skin of red onion using low-boiling polar solvents. ROSE has been used as an antioxidant and peroxide inhibitor in edible oils, to delay rancidity [13]. The authors attributed the greater peroxide inhibition efficiency of crude ROSE compared to its benzoylated derivative to the free hydroxyl groups of quercetin in crude underivatized ROSE. Due to the metal chelating properties of quercetin [15, 16, 17], which is also important for gum inhibition, ROSE as well as ROSE-formaldehyde resin have been applied as a corrosion inhibitors for zinc and mild steel respectively in acidic media [18, 19]. Azo-metal complexes derived from ROSE have also been investigated for their tanning properties [20]. The synthesis of Fe(III) and Cu(II)-ROSE-azo-complexes for application as pigments in surface coatings in oilfield environments has recently been reported [21, 22].

In this study, the performance of crude ROSE and commercial catechol as gum inhibitors for gas condensate is evaluated. Previously, butylated hydroxyanisole and phenylenediamine had been used to inhibit gum formation in gas condensates but it was clear that the cost implications would be a deterrent due to the high dosages (> 300ppm) of the commercial antioxidants required for effective inhibition [7]. This forms the motivation to investigate ROSE, a locally abundant, natural material as a potential alternative.

2. MATERIAL AND METHODS / EXPERIMENTAL DETAILS / METHODOLOGY

2.1 Sample Collection

Eight condensate samples with tendency for gum formation were collected from two different producing fields in the Niger Delta. Six samples were collected from gas wells and two from slug catcher. The samples were labeled A – H.Red onion skin was obtained from a vendor at fruit and vegetable garden market, Port Harcourt.

2.2 Preparation of Red Onion Skin Extract and Gum Inhibitor Formulation

ROSE was obtained following the method outlined by [23] with slight modification. The red onion skin was sun dried then ground to powder using a food blender. The powdered onion was extracted with 80% ethanol for 72h at room temperature. The mixture was filtered and solvent evaporated under vacuum. A dark red powder was obtained at a yield 17.3%w/w with respect to the starting material. A 1000ppm stock solution of the extract in diethyl ether was prepared.

2.3 Characterization of Condensates

The specific gravity (dry and wet) and API gravity of the condensate samples was determined according to ASTM D1298. Water-cut was determined by Dean-Stark distillation (ASTM D 4006-11). The asphaltene content of condensate was determined by ASTM D6560-12. Heavy metal content analysis was carried out by Flame Atomic Absorption Spectrophotometry (AAS) (ASTM D4691) using a Savant Atomic Absorption Spectrophotometer (GBC scientific Equipment). The concentration of iron, copper, zinc and manganese was determined.

2.4 Determination of Boiling Point Range

The boiling point range of the condensate samples was determined by ASTM D7169 using an Optidist distillation unit (PAC instruments). The test was carried out to determine the percentage of sample that will not boil under conditions for the gum test. 100ml of condensate sample was distilled under atmospheric pressure and percentage residue determined.

2.5 Gas Chromatography Analysis

The paraffin composition of condensate samples was determined by gas chromatography (GC) (ASTM D3328) using an Agilent 7890A gas chromatograph. 1µl of sample was auto-injected at an inlet temperature and pressure of $250^{o}C$ and 18.54psi.Helium gas at a flow rate of 0.455ml/min carried the sample at 15.0cm/sec through a 50m capillary column with internal diameter of 0.2mm and 0.5µm-thick film at a maximum temperature of $325^{o}C$. The eluates were detected on a flame ionization detector maintained at column temperature.

2.6 Gum content Analysis

Gum content of the condensate was determined by ASTM D381 -12 test method using an existent gum evaporation bath (Koeller Instruments Co. Inc.). Oxidative evaporation of 50 ± 0.5 ml of condensate sample was carried out at a temperature of 160 - $165^{o}C$ and air flow rate of 1000 ± 150ml/s. The deposit was washed with 25ml of heptane to obtain the washed gum content.

2.7 Performance Evaluation of ROSE as Gum Inhibitor

Seven condensates samples (A, B C, D, F, G, and H) were treated with ROSE solution at a dosage of 200ppm and 500ppm respectively. The dosed condensate was allowed to stand for 1 hour after which the gum content was determined. The gum content analysis was repeated under the same conditions as the untreated condensates. An identical evaluation was also carried out using catechol at 200ppm and 500ppm respectively.

3. RESULTS AND DISCUSSION

3.1 Characterization of Condensate Samples

Table 1 shows some of the physico-chemical properties of the condensate samples. Most of the condensate samples had negligible water content (dry) with the exception of samples A and D. The condensate samples have high API gravities (> 54) with the exception of A. Its low API gravity (determined based on dry specific gravity) is related to asphaltene content. The API gravity of sample D is higher than A, despite having higher asphaltene content, this is probably due to relatively higher abundance of light end paraffin in sample D. The iron, copper, zinc and manganese content of the condensate samples were all low, below the detection limit of 0.01mg/kg. Trace levels of heavy metal are sufficient to facilitate gum formation [1].

Table 1. Physico-chemical Properties of Condensate samples

Condensate sample	Field	Sp. gravity (wet) 15/15C	Sp. gravity(dry) 15/15C	API gravity	Water cut (%)	Asphaltene content (%)
A	1	0.8049	0.8048	44.3	0.05	0.25
B		0.7426	0.7425	59.1	0.025	0.044
C	2	0.7328	0.7327	61.6	0.025	0.021
D		0.7699	0.7573	55.3	10.4	0.395
E		0.7294	0.7294	62.5	0.025	0.008
F		0.7393	0.7393	59.9	0.025	0.03
G		0.7615	0.7614	54.3	0.025	0.042
H		0.7534	0.7533	56.3	0.025	0.038

3.2 Paraffin Composition of Condensates

Chromatograms of the condensate samples are shown in Fig. 1 – 7. Samples A and D contain light and heavy paraffinic ends in the range C6 – C30+.While sample G contains C28+ fractions, the concentrations of the heavier ends are very low. Samples C, E, F, H contain mainly light paraffinic ends and their chromatogram show a maximum paraffin carbon number between C-14 to C-16. Paraffin composition of condensates varies with the well and operational conditions.

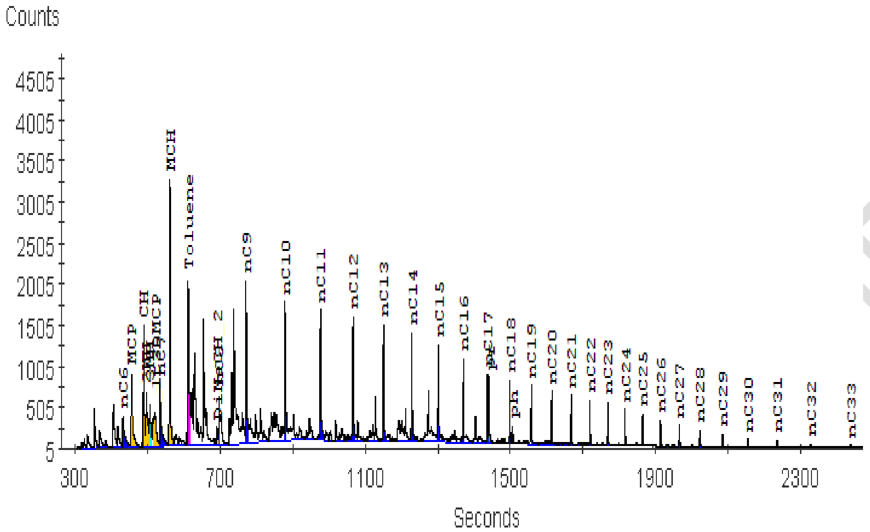

Fig. 1. GC-FID chromatogram of condensate A

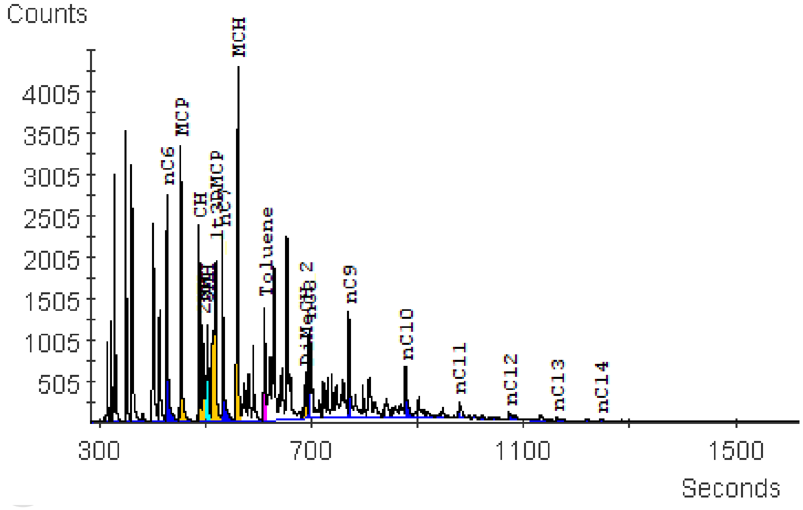

Fig. 2. GC-FID chromatogram of condensate C

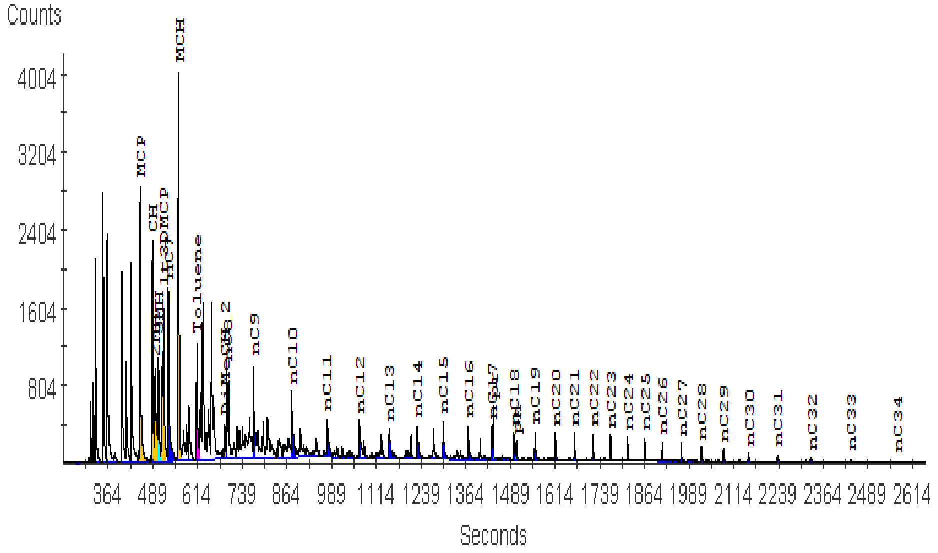

Fig. 3. GC-FID chromatogram of condensate D

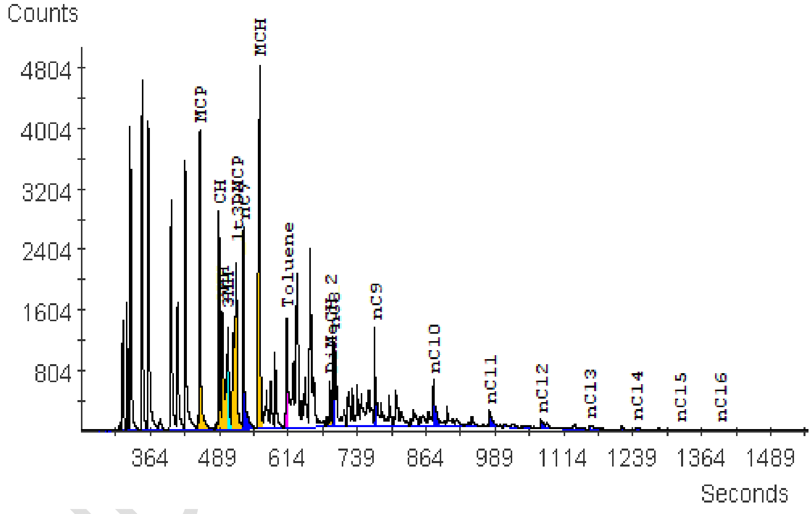

Fig. 4. GC-FID chromatogram of condensate E

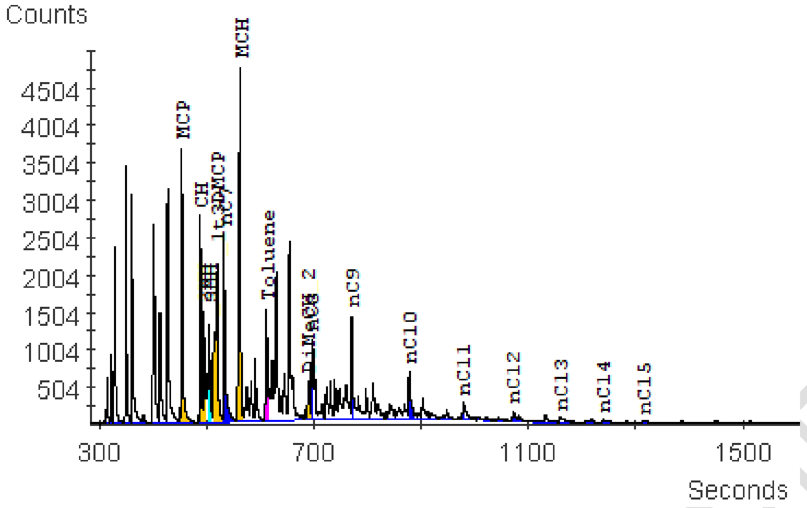

Fig. 5. GC-FID chromatogram of condensate F

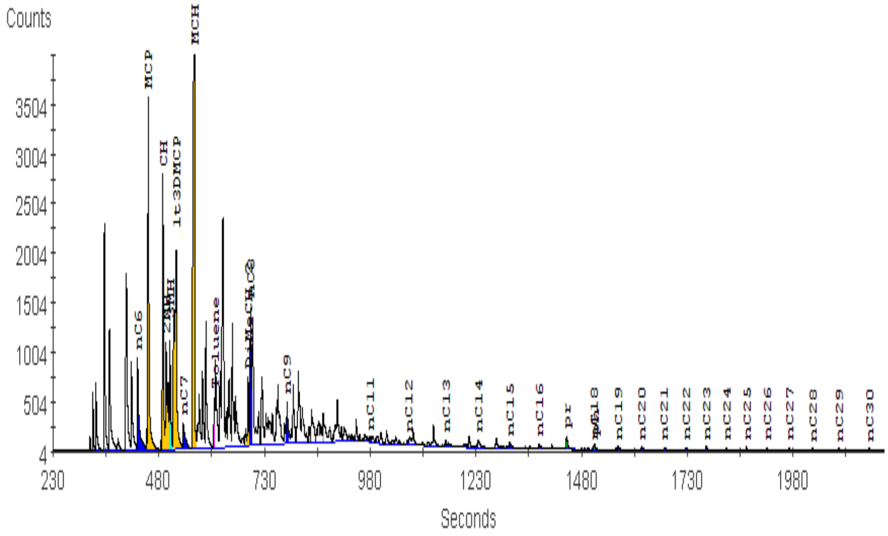

Fig. 6. GC-FID chromatogram of condensate G

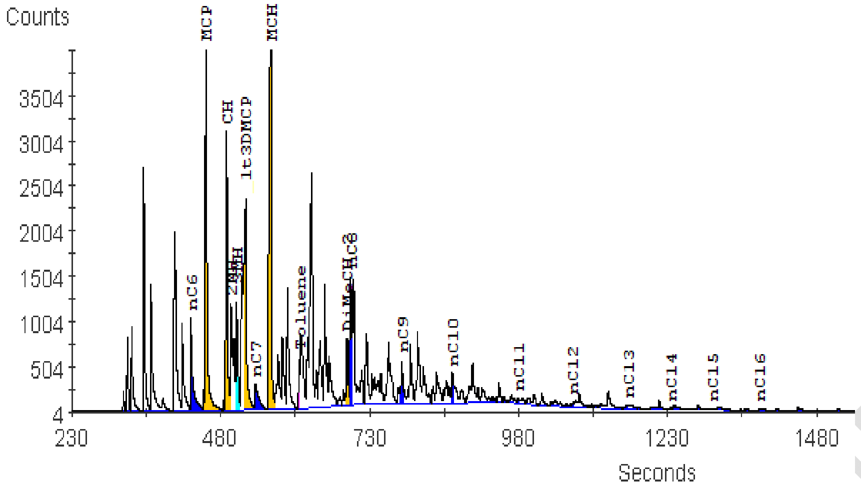

Fig. 7. GC-FID chromatogram of condensate H

3.3 Boiling Point Range

Fig. 8 shows the boiling point range of condensate samples. Sample A contains higher boiling fractions in line with its low API gravity. With the exception of sample D, with only 80% recovery, the % residue after distillation is low and ranges from 1.1% in sample C to 1.5% in sample A. Sample D has high content of non-volatile materials but also lower-boiling light end paraffin. The boiling point ranges correlate with the chromatographic data and consistent with the earlier observation on effect of paraffin and asphaltene content on API gravity. The condensates with heavier paraffin fractions boil at higher temperature.

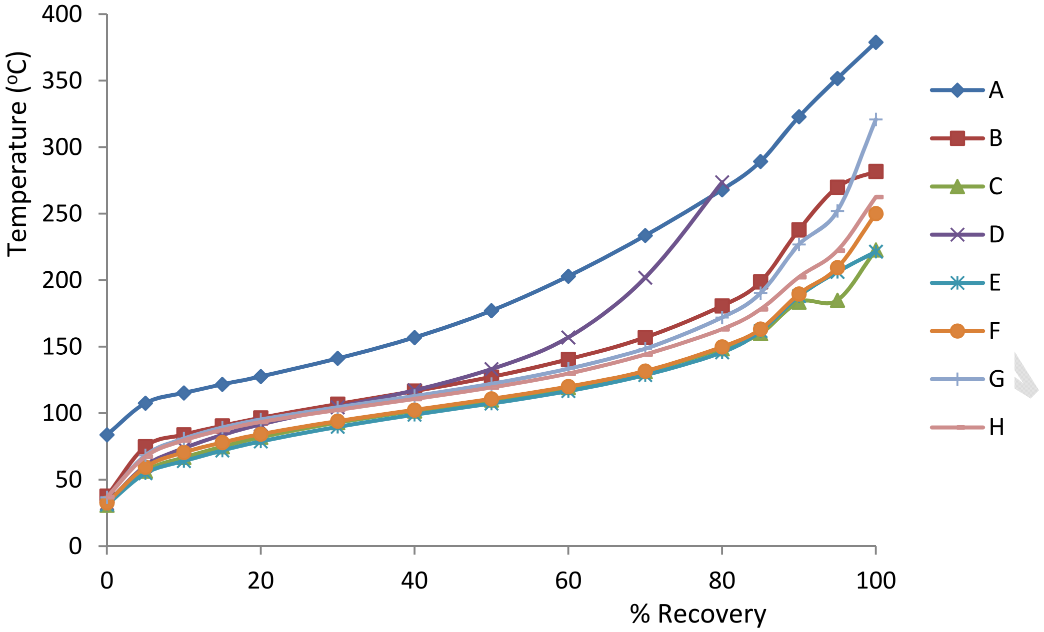

Fig. 8. Boiling point range of condensate samples

3.4 Gum Inhibition Tests

Washed and unwashed gum content of the condensate samples show that most of the unwashed deposits contain large quantities of non-gum material especially samples A, D and G (Table 2). This is probably due to heavier paraffin fractions in the condensate samples which do not evaporate under the conditions for gum test. Washed gum content is apparently a more suitable parameter for evaluation of gum formation tendencies in condensates using ASTM D381. The more asphaltic condensates generally have higher unwashed and washed gum content (Table 1 & 2). The presence of asphaltenes and resins in condensate increases its gum formation tendency. The gum inhibition efficiency of red onion skin extract and catechol are approximately equal in sample A, irrespective of dosage, with % gum inhibition > 99%. The inhibitors exhibit selectivity to condensate samples, but maximum and minimum gum inhibition efficiency (approximately 99.5% and 17% respectively) for both inhibitors is observed in the same condensate samples (A and G respectively) suggesting similar inhibition mechanism (Fig. 9). ROSE inhibited gum formation more effectively than pure catechol in three out of seven samples tested. Their performance in sample A was equal. Generally % gum inhibition was observed to increase with dosage, but in some condensates 200ppm of inhibitor was optimal for gum inhibition and increasing dosage had little or no effect on performance.

Table 2. Unwashed gum and washed gum content of untreated condensate samples

Condensate Sample	Gum content Unwashed gum (mg/100ml)	Washed gum (mg/100ml)
A	6541.8	644.2
B	38.2	4.4
C	23.4	1.4
D	15308.2	10334.6
E	2.2	0.6
F	540.2	8.0
G	1892.2	201.6
H	375.0	33.6

Table 3. Unwashed gum and washed gum content of condensates treated with ROSE

Condensate	200ppm ROSE		500ppm ROSE	
Sample	Unwashed gum (mg/100ml)	Washed gum (mg/100ml)	Unwashed gum (mg/100ml)	Washed gum (mg/100ml)
A	4385.2	2.8	3944	3.4
B	19.8	3.0	17.6	2.0
C	14.0	0.8	14.0	0.6
D	4961.8	1920.2	2823.3	395.4
F	234.8	4.6	218.0	2.0

G	825.0	166.4	502.4	85.6
H	177.4	6.6	150.2	0.8

Table 4. Unwashed gum and washed gum content of condensates treated with catechol

Condensate	200ppm Catechol		500ppm Catechol	
Sample	Unwashed gum	Washed gum	Unwashed gum	Washed gum
	(mg/100ml)	(mg/100ml)	(mg/100ml)	(mg/100ml)
A	6336.2	3.4	4766.6	3.0
B	16.4	1.6	16.0	1.0
C	14.2	0.2	13.2	0.6
D	6856.0	4084.8	6813.6	3852.8
F	448.4	6.0	329.8	5.6
G	1456.8	167.0	1216.8	24.0
H	317.4	24.4	242.6	8.0

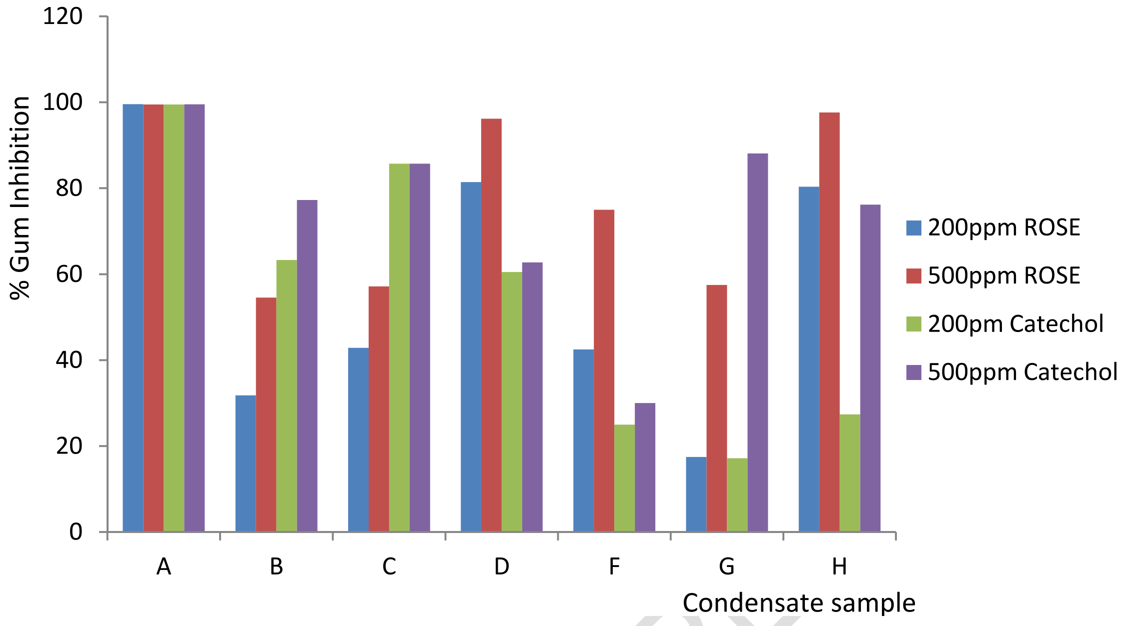

Fig.9. Percent Inhibition in washed gum content of condensate treated with ROSE and Catechol

4. CONCLUSION

Red onion skin extract (ROSE), a quercetin-rich natural antioxidant has been found to inhibit the formation of gum in washed and unwashed state in condensates. The gum inhibition efficiency of crude ROSE is comparable to catechol, a conventional antioxidant of similar chemistry at 200ppm. Antioxidants exhibit selectivity in gum inhibition to condensates from different wells. Determination of asphaltene content in condensates provides useful information for evaluating gum formation tendencies. Red onion skin extract is a potential substitute for conventional antioxidants used in gum inhibition, which are expensive. There is need for further work to investigate other low-cost sources of naturally occurring anti-oxidants that can inhibit gum in condensate even at lower concentrations for cost effectiveness.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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