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Chemical Composition and Cold Flow Property of Cottonseed Oil Biodiesel Fuel

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Abstract

The Cottonseed oil methyl ester (COME) was prepared using an alkali - catalyzed trans esterification reaction, and its chemical composition and cold flow properties (CFP) were studied. Two approaches, viz. blending with petrodiesel and treating with cold flow improver (CFI) were used to improve the CFP of COME. The results showed that COME was mainly composed of fatty acid methyl esters (FAMEs): C14:0–C22:0, C16:1–C20:1, C18:2 and C18:3–C20:3. The mass fractions of saturated and unsaturated FAMEs were 27.69% and 71.65%, respectively. The cold filter plugging point (CFPP) and kinematic viscosity (KV) at 40 °C of COME are -1 °C and 4.63 mm2/s respectively. Blending with -10 petrodiesel (-10PD) and 0 petrodiesel (0PD) can decrease the CFPP of COME/-10PD (B30-B40) and COME/0PD (B40-B50) -12 and -8 ℃ respectively. With the increase in petrodiesel content, the KV at 40 ℃ of blending oil decreased, and viscosity-temperature characteristics of blending oil were improved. When used Flow Fit (≤3vol.%), the CFPPs were reduce from COME/-10PD B5, B7, B10, B20, B50 and COME -8, -8, -9, -11, -11 and -1 °C to -28, -27, -26, -25, -16 and -5 °C respectively; COME/0PD -3, -3, -4, -5, -8 and -1 °C to -26, -25, -24, -24, -16 and -5 °C respectively.

Keywords*: Biodiesel, Cold flow property, Cold filter plugging point, Kinematic viscosity.*

1. Introduction

There has been renewed interest in the use of biodiesel due to its environmentally friendly and renewable nature as against the petrodiesel (PD), which is a fossil fuel leading to a potential exhaustion, increasing prices of crude oil and environmental concerns. In addition, the development of biodiesel may also reduce the dependence on fuels derived from imported petroleum, which continue to decrease in availability and affordability. Presently, commercial biodiesel is mainly produced from edible oil, such as rapeseed, soybean and palm oil. Therefore, biodiesel is confronted with a severe challenge for petrol fuel because of expensive feedstock cost and increasingly aggravating tension between energy crisis and food security. In China, with abundance of cotton resources (an annual production of about 7 million tonnes), there are a high amount of inedible cottonseed oil, which have great potential for making biodiesel to supplement other conventional sources [1,2].

Biodiesel's performance may restrict its commercial viability during cold weather in moderate climates. There is evidence that fatty acid methyl esters (FAMEs) derived from cottonseed oil and methanol develop performance issues when ambient temperatures

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approach 0 °C. As temperatures fall into this range, saturated fatty acid methyl esters (SFAMEs) in cottonseed oil methyl ester (COME) begin to nucleate and form solid crystals. These crystals plug or restrict flow in fuel lines and filters during start-up and can lead to fuel starvation and engine failure. This limit agrees well with those predicted in bench-scale cold filter plugging point (CFPP) test studies. Given that the analogous limitation for -10 petrodiesel (-10PD) and 0 petrodiesel (0PD) fuel are -10 and 0 °C respectively, it follows that the cold flow property (CFP) of methyl esters from vegetable oil will preclude widespread commercialization as fuels in moderate temperature climates such as those in central and eastern China.

One recent report [3] showed that a linear correlation exists between FAMEs composition and CFPP. That is, CFPP increases linearly with the increase of the content of SFAMEs and the length of the carbon chains; CFPP decreases linearly with the increase of the content of unsaturated fatty acid methyl esters (UFAMEs) and the unsaturated degree. According to chemical compositions and theirs melting point (MP), biodiesel may be considered a mixture of high-MP SFAMEs dissolved in low-MP UFAMEs. Formulating FAMEs such as admixture or crystallization fractionation may be approaches for improving CFP of biodiesel with minimal increase in cost [3, 4-10]. Biodiesel with high SFAMEs content such as palm oil methyl ester (POME, SFAMEs: 40.13wt.%, CFPP: 10 °C) or may be admixed with FAMEs with more forgiving CFP such as rapeseed oil methyl ester (ROME, SFAMEs: 6.49wt.%, CFPP: -9 °C). A 3/7 (vol) POME/ROME (CFPP: -1 °C) admixture was reported to have CFP comparable to neat POME [3]. Similar results were observed for tobacco seed oil methyl ester (TSOME)/waste mixed cooking oil methyl ester (WMCOME) admixture [11]. Also, crystallization fractionation to reduce long-chain SFAMEs content may be effective in decreasing CFPP of biodiesel [8-10]. The process is performed in two steps, crystallization and separation of liquid and solid fractions. Yield defined by separating high- and low-MP fractions depends on maintaining control during both steps.

Other studies confirmed that blending with petrodiesel fuel [11-14] and treating with cold flow improver (CFI) [12, 14-16] significantly reduce cloud point (CP) / pour point (PP) / CFPP. Chuang-Wei Chiu et al. [12] studied the CFP of soybean oil methyl ester (SOME) and their biodiesel/low sulfur diesel (LSD #2) or kerosene blends. Blending with LSD #2 decreases CP and PP, from SOME -1 and -6 °C to B80 -5 and -15 °C, respectively; and blending with kerosene also decreases CP and PP to B20 -15 and -21 °C, respectively. Rushang M. Joshi et al. [13] studied the CFP of fish oil ethyl esters (FOEE), no.2 diesel fuel, and their blends. Increasing blend ratio of FOEE/no.2 diesel fuel blends resulted in a linear increase in CP and PP.

In this study, the CFP of COME is researched on the basis of the determination of its chemical composition with gas chromatography-mass spectrometer (GC-MS). In addition, two approaches for improving CFP of COME are investigated, including: blending with petrodiesel fuel and treating with CFI additives.

2. Materials and Methodology

2.1 Materials

Cottonseed oil is purchased from Dantu grain and oil chemical plant, China. -10PD and 0PD are obtained from China Petroleum & Chemical Corporation, China. Flow Fit is provided by Liqui Moly, German. All the chemicals used are analytical reagent grade. Used as a standard for chromatographic analysis, methyl heptadecanoate (P99.5% purity) is bought from Sigma-Aldrich, USA.

2.2 Apparatus

The main apparatus used include a TraceMS GC-MS (Finnigan Corp., USA); a SYP1026-1 Density tester, a SYP1003-6 kinematic viscosity tester, a SYP1003-7 low temperature kinematic viscosity tester, a SYP1002z-3 flash point tester, a SYP2007-I cold filter plugging point tester, and a SYP 1017-1 copper strip corrosion tester (Shanghai BOLEA Instrument & Equipment Co. Ltd., China); a FLASH EA-1112A elemental analyser (Thermos Corp., Italy).

2.3 Biodiesel Preparation

COME is prepared from cottonseed oil using an alkali-catalyzed transesterification method. The cottonseed oil is transesterified with methyl alcohol to produce the biodiesel. The volume ratio of methyl alcohol to the cottonseed oil is set at 1:5. In this reaction 0.8 wt.% of NaOH in relation to oil is dissolved in methanol, and then added to the oil being stirred at 55 °C for 80 min. After standing and layering, the mixture is decanted, and the lower layer, rich in glycerol and methanol, is removed. The top layer is washed with water three or four times to remove residual NaOH, methanol, and soap. The washed biodiesel is dried at 48 °C for about 5 min.

2.4. Analytical Method

The oil sample chemical composition is analyzed with a Finnigan GC-MS system equipped with a DB-WAX capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) (Trace-Ultra/DSQ; Thermo Electron Co., Waltham, USA) and FDI. Helium is used as the carrier gas at a flow rate of 0.8 ml/min. Electron ionization mode (electron energy of 70 eV) is used for GC-MS detection. Sample injection volume is 0.1 µl. Temperature is programmed as follows: 180 °C maintained for 0.5 min; 6 °C/min from 180 to 215 °C; and 3 °C/min from 215 to 230 °C maintained for 13 min.

Density, KV, flash point, CFPP, sulfur content and copper strip corrosion are determined according to GB/T 13377-2010, GB/T 265-1988, GB/T 261-2008, SH/T 0248-2006, SH/T 0689-2000 and GB/T 5096-1985, respectively.

3. Results and Discussion

3.1. Characterization of Samples

The fuel properties of COME obtained following the above-mentioned procedure are summarized in Table 1 along with -10PD and 0PD. It can be seen that COME had fuel properties comparable to those of -10PD and 0PD were within the limits prescribed in the GB/T 20828-2007 standards for biodiesel.

3.2 Chemical Composition

The chromatogram of COME, -10PD and 0PD analyzed by GC-MS is showed in Fig. (1).–Fig. (3). and the main chemical compositions are showed in Table 2-Table 3.

COME is mainly composed of FAMEs of 14–22 even number carbon atoms, including SFAMEs ($C_{14:0}$–$C_{22:0}$) and UFAMEs ($C_{16:1}$–$C_{20:1}$, $C_{18:2}$ and $C_{18:3}$–$C_{20:3}$) with mass fractions of 27.69% and 71.65% respectively. -10PD is mainly composed of the n-alkenes of 8–26 carbon atoms, and 0PD is mainly composed of the n-alkenes of 10–22 carbon atoms.

3.3 Cold Flow Property

Cold filter plugging point:The CFPP of COME, -10PD and 0PD were -1, -7 and -3 °C, respectively. The CFP of COME is poorer than that of -10PD and 0PD. Biodiesel may be considered a pseudobinary solution consisting of high-MP SFAMEs and low-MP UFAMEs. SFAMEs content in COME reaches up to 27.69wt.%. As temperatures fall, SFAMEs in COME begin to nucleate, form solid crystals and agglomerate. The CFPP of biodiesel increases with SFAMEs amount increasing. When the SFAMEs content is high, biodiesel is easier to crystallize, the CFPP of biodiesel is high, and the CFP would be poorer. This may restrict the application of COME during cold weather. So it is very necessary to reduce the CFPP of COME.

Kinematic viscosity:The KV at 40 °C of COME, -10PD and 0PD are 4.63, 2.53 and 2.91 mm^2/s respectively, which are within the limits prescribed (1.9-6.0 mm^2/s) in the GB/T 20828-2007. Viscosity-temperature characterization curves of COME, -10PD and 0PD are shown in Fig. (4). It can be seen that comparing with -10PD and 0PD, KV of COME is higher at the same temperature. It is mainly because of the difference between the chemical composition of COME and -10PD or 0PD which made the average molecular weight of COME higher than -10PD and 0PD. The content of the long-chain SFAMEs is high in COME. So it is easier to crystallize at low temperature. And its KV is higher than -10PD and 0PD.

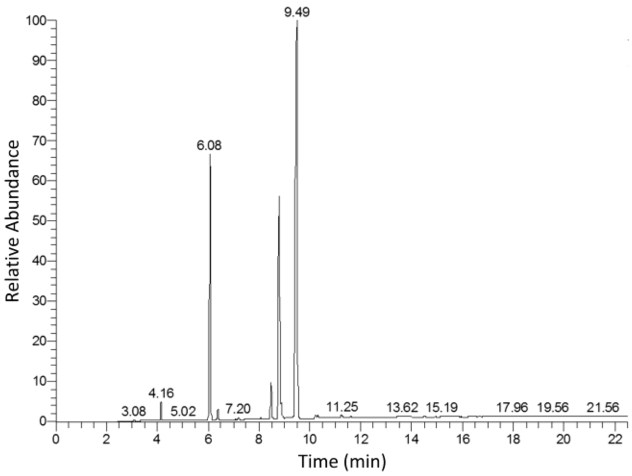


Figure 1. The Gas Chromatogram of COME

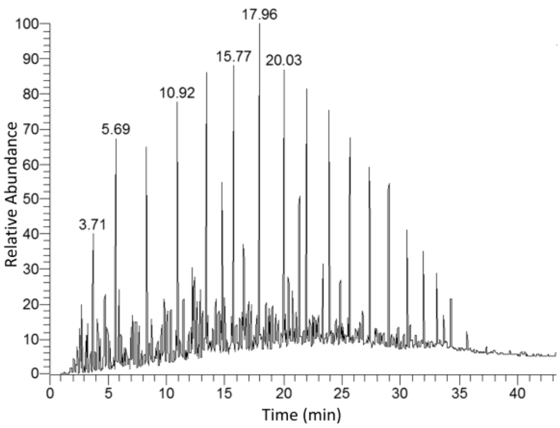


Figure 2. The Gas Chromatogram of -10PD

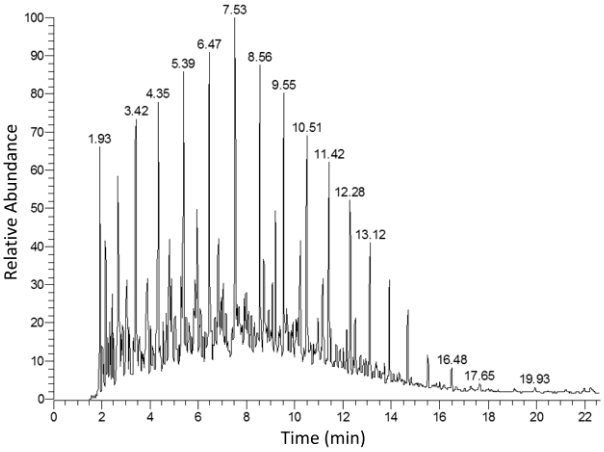


Figure 3. The Gas Chromatogram of 0PD

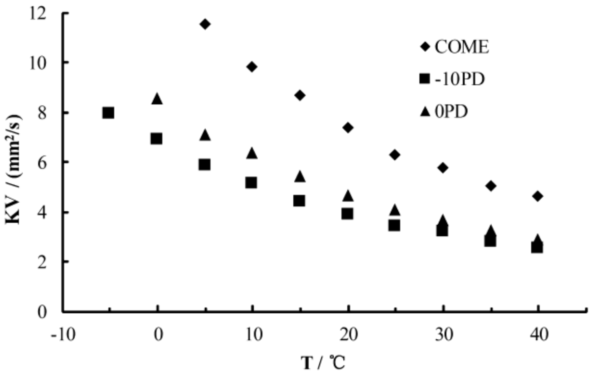


Figure 4. The Viscosity-temperature Relationship of COME, -10PD and 0PD

It also can be seen that the KV of COME, -10PD and 0PD increases with temperature decreasing. It is because with temperature decreasing, the intermolecular interaction of COME, -10PD and 0PD increases, so does the internal friction and the KV of COME, -10PD and 0PD. The average molecular weight of COME is higher than -10PD and 0PD, so the intermolecular interaction of COME is also higher. In addition, the SFAMEs in COME are easy to crystallize and form a three-dimensional expended framework. It may cause faster growth of KV than -10PD and 0PD.

Table 1. Fuel Properties of COME, -10PD and 0PD

Property	Unit	COME	-10PD	0PD	GB/T 20828-2007	
					Min.	Max.
Density (20°C)	kg/m^3	881	833	845	820	900
Kinematic viscosity (40°C)	mm^2/s	4.63	2.53	2.91	1.9	6.0
Flash point	°C	155	61	63	130	-
CFPP	°C	-1	-7	-3	-	-
Sulfur content	wt.%	0	0.16	0.17	-	0.005
Copper strip corrosion (50°C; 3 h)	Rating	1	1	1	-	1

Table 2. Main Composition of Biodiesel of COME

COME	$C_{14:0}$	$C_{16:0}$	$C_{18:0}$	$C_{20:0}$	$C_{22:0}$	$C_{16:1}$	$C_{18:1}$	$C_{20:1}$	$C_{18:2}$	$C_{18:3}$	$C_{20:3}$
Content / wt.%	0.98	23.36	2.90	0.30	0.15	0.72	19.54	0.10	50.96	0.26	0.07

NOTE: $C_{m:n}$ is the shorthand of FAME; *m* means the carbon number of fatty acid; *n* means the number of C=C.

Table 3. Main Composition of Biodiesel of -10PD and 0PD

Content / wt.%	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}	C_{21}	C_{22}	C_{24}	C_{26}
-10PD	0.36	1.75	5.51	4.09	6.70	2.24	4.37	12.69	3.83	6.65	1.38	0.81	1.35	8.52	0	0.74	0.27
0PD	0	0	5.85	9.91	7.88	1.80	6.42	6.91	9.15	3.76	6.53	6.41	3.97	3.92	2.59	0	0

NOTE: C_m is the shorthand of alkane; *m* means the carbon number of alkane.

3.4 Improvement of Cold Flow Property

Blending with -10 petrodiesel and 0 petrodiesel:Although most of the properties of biodiesel fuels are comparable with that of petrodiesel fuel but CFPP which indicate the cold flow behavior of a fuel is poor. Fig. (5). shows the reduction in CFPP of COME when blended with -10PD and 0PD.

The CFPP of blending oil decreases first and then increases with COME addition amount rising, and arrives at extreme values, viz., COME/-10PD, B30-B40, CFPP = -12 °C;and COME/0PD, B40-B50, CFPP = -8 °C. It is because blending with -10PD and 0PD would decrease the relative content of SFAMEs in COME and make it difficult to crystallize. Therefore, the CFPP of blending oil is lower than COME. In addition, the SFAMEs in COME can form a eutectic mixture with the long-chain n-alkane in -10PD and 0PD (Table 3), which would make the CFPP of blending oil lower than COME and -10PD or 0PD. The CFPP of COME/-10PD and COME/0PD can be reduced to -12 and -8 °C respectively. Adding -10PD and 0PD have changed the composition of COME. The size and shape of the crystals also have been changed under low temperature. It can effectively prevent the formation of three-dimensional network structure.

Viscosity-temperature characterization curves of blending oil are shown in Fig. (6).. It is shown that the KV of blending oil decreases with increasing content of COME, and blending oil KV lies between -10PD or 0PD and COME. With temperature decreasing, KV of blending oil increases, and when the temperature is close to CFPP, the blending oil KV would leap. The viscosity-temperature characterization curves of B5-B10 would close up to that of -10PD or 0PD. It is because the average molecular weight of COME is greater than -10PD or 0PD, and the KV of COME is also greater than -10PD or 0PD. With the increasing of COME addition, the average molecular weight of blending oil increases gradually, and the KV of blending oil also presents a gradually increasing trend. With temperature decreasing, the blending oil crystallizes gradually. Solid-liquid phase transition occurs, which enhances the intermolecular forces and makes the viscosity-temperature characterization curves of blending oil increased gradually.

B5-B10 has little effect on the average molecular weight of blending oil. The viscosity-temperature characterization curves of blending oil are close to that of -10PD or 0PD. This suggested that B5-B10 hardly affects KV of petroleum diesel, and the blending oil could meet the requirement of CFP.

Blending with petroleum diesel not only can decrease the CFPP of COME, but also decrease the KV of COME and improve its CFP in some extent. So COME can partly substitute petroleum diesel, this can ease global petroleum crises to some extent.

Treating with cold flow improver: The effect of Flow Fit on CFPP of the blending oil is shown in Table 4. It can be seen that addition of Flow Fit (≤3.00vol.%) can reduce the CFPP of blending oil from COME/-10PD B5, B7, B10, B20 B50 and COME -8, -8, -9, -11, -11 and -1 °C to -28, -27, -26, -25, -16 and -5 °C respectively; COME/0PD -3, -3, -4, -5, -8 and -1 °C to -26, -25, -24, -24, -16 and -5 °C respectively. B5-B20, adding the Flow Fit with a content of 1.00vol.% can reduce the CFPP of blending oil and improve its CFP significantly. This is because the main composition of Flow Fit is alkyl aromatics whose long-chain alkyl group may form co-crystal with long-chain SFAMEs in COME, so it can suppress the grain growth of crystal. Through the adsorption on crystal surface, Flow Fit can prevent the growth of crystal in COME and its blending oil. In addition a little of Flow Fit which does not adsorb can serve as nucleus, and form small crystals. This would make it difficult to form a three-dimensional network structure in the oil. Therefore, the CFP of COME and its blending oil will not be affected by crystals.

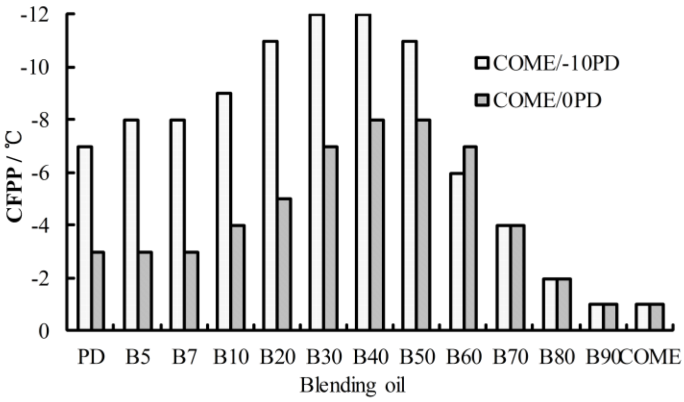
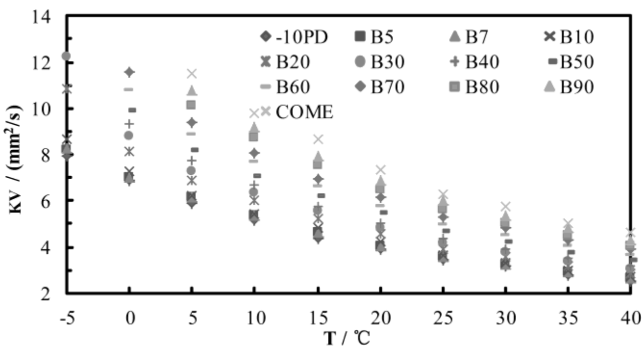
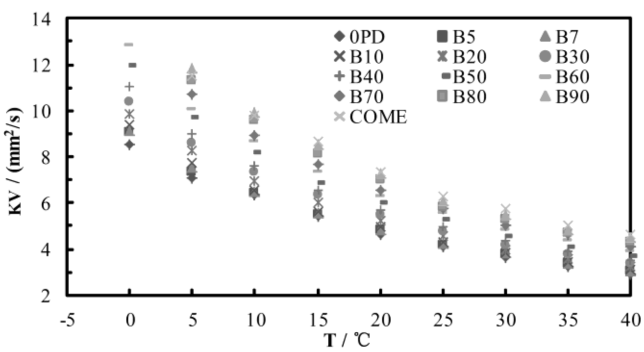


Figure 5. CFPP of Blending Oil



a. -10PD



b. 0PD

Figure 6. The Viscosity-temperature Relationship of Blending Oil

Table 4. CFPP of Blending Oil without/with Flow Fit

Blending Oil	COME/-10PD			COME/0PD		
	Flow Fit /vol.%	CFPP without Flow Fit /°C	CFPP with Flow Fit /°C	Flow Fit /vol.%	CFPP without Flow Fit /°C	CFPP with Flow Fit /°C
B5	0.15	-8	-28	0.15	-3	-26
B7	0.30	-8	-27	0.30	-3	-25
B10	0.30	-9	-26	0.50	-4	-24
B20	0.50	-11	-25	0.90	-5	-24
B50	1.00	-11	-16	1.90	-8	-16
COME	3.00	-1	-5	3.00	-1	-5

4. Summary

The above discussion shows that:

(1) The main chemical composition of COME is FAMEs composed of 14 to 22 even-numbered carbon atoms, including SFAMEs ($C_{14:0}$–$C_{22:0}$) and UFAMEs ($C_{16:1}$–$C_{20:1}$, $C_{18:2}$ and $C_{18:3}$–$C_{20:3}$) with mass fractions of 27.69% and 71.65% respectively. The CFPP and KV at 40 °C of COME are -1 °C and 4.63 mm^2/s respectively, and comparing with -10PD and 0PD, viscosity-temperature characteristics of COME are poorer. COME has poor CFP.

(2) Blending with -10PD and 0PD can reduce the CFPP and KV of blending oil fuel to a certain degree, and can improve viscosity-temperature characteristics, raising the possibility that petrodiesel can be partly replaced with COME for use in low temperatures. COME/-10PD, B30-B40, CFPP = -12 °C, and COME/0PD, B40-B50, CFPP = -8 °C.

(3) The addition of Flow Fit can decrease the CFPP of COME, COME/-10PD and COME/0PD from COME/-10PD B5, B7, B10, B20, B50 and COME -8, -8, -9, -11, -11 and -1 °C to -28, -27, -26, -25, -16 and -5 °C respectively; COME/0PD -3, -3, -4, -5, -8 and -1 °C to -26, -25, -24, -24, -16 and -5 °C respectively.

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