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Analytical Studies on the Quality and Environmental Impact of Commercial Motor Gasoline available in Multan region of Pakistan

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Abstract

Physico-chemical characteristics such as specific gravity, reid vapour pressure, copper corrosion, distillation (I.B.P., F.B.P., Total recovery & residue) and hydrocarbon contents (saturates, aromatics and polars) of gasoline of different oil marketing companies collected from retail outlets in district Multan have been analysed using standard ASTM procedures. Results have been compared with the Pakistani, Indian and European specifications to assess the quality of Pakistani gasoline (petrol). The environmental impact of gasoline has also been assessed.

Keywords: *Quality, Aromatics, PS specification, Environmental impact.*

Introduction

The term Gasoline, an American term, is used widely in USA and the word Petrol is used in Britain for motor fuels. This product is usually associated with fuel available at car service station. Gasoline [1] consists of organic compounds containing carbon and hydrogen (hydrocarbon). Substances derived from crude oil have great commercial value. The customary processing of crude oil does not involve the separation and handling of pure hydrocarbons. The products derived from crude oil are always mixtures, occasionally simple, but more often very complex. Gasoline is a complex mixture of hydrocarbons that normally boils below 355°F (180°C) or at the most, below 390°F (200°C). The hydrocarbon constituents in this range are those that have 4 to 12 carbon atoms in their molecular structure. These hydrocarbons fall into three categories such as paraffins, olefins and aromatics [2]. Automotive gasoline has been classified into two grades, premium and regular on the basis of octane number. Gasoline with higher octane number has numerous benefits including reduced exhaust emissions [3] and engine noise, improved cold starting and engine durability. Quality [4,5] of motor gasoline is generally determined by measuring its various physico-chemical parameters such as specific gravity, octane number, distillation range, residue, copper corrosion and sediments, etc.employing standard test methods [6,7].

Due to speedy mechanization in this era, there has been a tremendous increase in the number of light and heavy vehicles in Pakistan that has resulted in a very high demand for motor gasoline. The petroleum [8, 9] products have gained prime importance in our daily life. It has been noticed that some greedy petroleum [10] dealers exploit this essential need of the transport system and mix cheaper oils with these expensive products to earn more profit. There is a general complaint about the poor engine performance and increased exhaust emission by a considerable number of consumers from time to time. Consumers suspect the adulteration of different commercially available motor gasoline products. Keeping in view, the consumers complaints about poor quality of these commercial products, we thought it worthwhile to test the quality of different locally marketed brands of motor gasoline products.

The trend today is towards making gasoline more environment and human friendly or making

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gasoline a really clean fuel. Most petroleum refineries are facing the challenge of producing motor gasoline having all the desirable properties and also complying with the ever-increasing environmental regulations and health restrictions on automotive emissions. The environmental regulations were created to guard against high levels of lead, aromatics, olefins and sulfur in gasoline, reduction in volatile organic compounds, toxic nitrogen oxides (NO_X) in automotive tailpipe emissions, and emissions at retail out lets.

Among the techniques, high-resolution capillary GC equipped with flame-ionization detection (FID) [11] and capillary GC-MS are the most important and most widely used techniques for separation, characterization, and identification of hydrocarbons present in gasoline. In the present study gasoline was fractionated into aliphatic, aromatic and polar hydrocarbons. Characterization and identification of individual aliphatic, aromatic, and polar was accomplished by using capillary GC with FID detector [12-17]. Fifty compounds were identified based on comparison of GC retention data with individual authentic standards.

Petroleum products contain toxic components and produce acute toxic effects, chronic toxicity and carcinogenity. They can foul shorelines and interfere with water treatment. Petroleum oils can cause devastating physical effects such as smothering, causing oxygen depletion, suffocation, egg contamination, destruction of existing and future food supply, affecting breeding animals and habitat. Petroleum oil spills can have a severe impact on drinking water resources. Oil pollution seriously damages the terrestrial and aquatic environment. It does not take a spill of catastrophic magnitude to have a serious impact on an aquatic habitat. The complex food chain or web, from microorganisms and plants to shellfish, mammals, and birds is affected by even small spills

Experimental

Commercially available motor gasoline samples were collected randomly from retail outlets of different marketing companies available in District Multan. Samples were tested using standard ASTM procedures. Distillation measurements, final boiling points (°C) and residual (% vol.) of motor gasoline samples were determined using ASTM D-86 method. Instrument used for distillation was manufactured by Gallenkamp, England. Specific Gravity 60/60^{o}F was measured by Glass Hydrometer (Poulten Selfe&Lee, England) following the ASTM method D-1298. Reid vapour Pressure (RVP) @37.8^{o}F was measured using ASTM method D-323. Copper Strip Corrosion @ 50^{o}C was measured by using Copper Strip and Copper Strip Corrosion Bomb & Bath (Koehler, USA) following the ASTM test method D-130. Hydrocarbons were measured by Perkin Elmer Model (8700) Gas Chromatograph.

Analysis of Hydrocarbons by Gas Chromatography

A 0.2-µL of each gasoline sample was injected without prior treatment to a Perkin Elmer (PE) 8700 gas chromatograph equipped with a flame-ionization detector (FID) with a 1-min purge-off. A Polar capillary column sp-2340 (60 m × 0.25mm) having stationary phase of methyl lignocerate was used. The carrier gas, nitrogen (3.5 ml/min) transported the vaporized sample through the column in which it partitioned into individual components, which were sensed by FID detector as they eluted from the end of the column. The detector signal was recorded with integrating computer. Each eluting component of each gasoline sample was identified by comparing its retention time with the retention time of reference standard under identical conditions (Table-1). Following temperature programme was used: Initial temperature70°C, Ramp rate 4°C per minute, Second temperature 120°C, Ramp rate 10°C per minute, Final temperature 220°C, Stay time 10 minute at 220°C.The concentration of each component in wt% was determined by measuring the peak area. The components were sum up as saturates, aromatics and polars.

Motor gasoline (Petrol) is an important fuel in human life but it is also responsible for deteriorating Ambient Air Quality (AAQ) through fugitive and exhaust emissions. Oxygenates help to reduce CO emission and they are excellent octane improvers. Oxygen limit at a maximum of 2-7 wt/wt % in the fuel is put by the international specifications. The US Clean Air Act of 1990 had specified that oxygenates must be added in the gasoline sold in 41 cities of US which were under non-attainment limit of CO. In Pakistan oxygenates are not used in gasoline and Ministry of Petroleum has not specified about oxygenates in petrol while European gasoline specification for oxygenates is 2-3 wt/wt % (Table-2) and Indian specification is 2-5 wt/wt % (max.) (Table-2). It means that oxygenates are not present in petrol.

Lower aromatics reduce the reactivity of emissions; produce less engine deposits and contribute to lower benzene emissions. Presently there are no limits for aromatics and olefins in Pakistani gasoline. European specification for olefins is 18 %v/v (max.) and for aromatics is 42 % v/v (max.) (Table-2) while Indian specifications for olefins are 10 %v/v (max.) and 35 %v/v aromatics (max) (Table-2). In future Pakistan may have to limit the aromatics up to a maximum of 35-40 % v/v or wt/wt %. Similarly, the limits for olefins at around 15-20 % v/v or wt/wt % may have to be implemented. In our study we have determined aromatics 43.19 wt %(table-3) in PSO gasoline, 42.35 wt % (Table-4) in SHELL gasoline and 32.98 wt % (Table-5) in CALTEX gasoline. These quantities of aromatics in Pakistani gasoline are high. PSO gasoline has been found paraffins (saturates) 32.34 wt % (Table-3), 39.74 wt % (Table-4) in SHELL gasoline and 41.68 wt % (Table-5) in CALTEX gasoline. The concentration of polars 7.830 wt %(Table-3) in PSO gasoline, 6.810 wt %(Table-4) in SHELL gasoline and 4.170 wt % (Table-5) in CALTEX gasoline while Indian standards have maximum 10 %v/v olefins and 35 % v/v aromatics. Pakistani gasoline has very high concentration of aromatics as compared to Indian gasoline and is not environmentally favorable. CALTEX gasoline has low concentration of aromatics (32.98 wt %) as compared to PSO and SHELL gasoline.

European and Indian standards have 1 % v/v benzene limit. The benzene (carcinogenic) concentration in Pakistani petrol sample is high which must be reduced and its limit should be specified by the PSQCA. The benzene concentration in PSO gasoline is 3.515-5.073 wt % (Table-3), 4.930-6.640 wt % (Table-4) in SHELL gasoline and 3.890-7.540 wt % in CALTEX gasoline (Table-5). These concentrations of benzene in petrol are very high. As discussed earlier, the concentration of total aromatic compounds must be decreased. The concentration of benzene and total aromatics show that Pakistani petrol is of not a good quality as compared to European gasoline. If aromatics concentration is reduced in gasoline then there will be problems that octane number of petrol will be reduced, that affects the performance of the engine. Aromatics are octane number boosting agents, and lower aromatics concentrations lower the octane number, and result in poor quality of petrol. Octane boosting compounds are not environmentally friendly because aromatics produce more smoke and smog. Olefins form engine fouling gums, more smoke and smog. Short-term effects of benzene and other aromatics include: Anemia, Nervous system disorders, Depressed immune system and Death when exposed to extremely high concentrations, Dizziness, Drowsiness, Rapid heart beat, Disorientation, Unconsciousness, Headaches, Giddiness, Loss of muscular control are other symptoms. Long-term effects include: Possible reproductive damage (Sex depression), Damage to chromosomes, Cancer, especially a type of leukemia known as acute myeloid leukemia (AML), Dermatitis. Ground Level Pollution includes: Ozone depletion, Greenhouse effect and Acid rain.

Specific gravity range of PSO petrol is 0.751-0.767 (Table-3), SHELL petrol is 0.754-0.760 (Table-4), CALTEX petrol is 0.755-0.762 (Table-5) and PS limit is 0.76(max.) (Table-2). On the basis of specific gravity all petrol samples are according to the prevalent Pakistan standard limits. Low specific gravity shows good quality of gasoline.

Lower RVP reduces vehicle evaporation emissions from fuel tanks, carburetor, running losses, and refueling emissions. Ried vapour pressure range of PSO petrol is 9.500-9.800 psi, SHELL petrol range is 9.700-10.00 psi, CALTEX petrol range is 9.500-9.900 psi and PS limit is 10 psi (max.) (Table-2). This data shows that SHELL petrol is of good quality. High Reid Vapour Pressure shows that there are high concentrations of light components. These light components give adequate vaporization of fuel air mix for easy engine cold start. Too many heavy components contribute to chamber deposits and spark plug fouling causing release of unburnt hydrocarbons into the atmosphere.

Copper strip corrosion of all these petrol samples is according to the PS limit (1 max.). It means that all the patrol samples are neutral.

In distillation, the final boiling point range of PSO petrol samples is 182.0-190.0^{o}C, SHELL petrol range is 180.0-182.0^{o}C, CALTEX petrol range is 185.0-188.0^{o}C and PS limit is 205^{o}C(Table-2).Lower value of final boiling point indicates good quality. It means that SHELL petrol is of good quality. Indian standard limit for final boiling point is195^{o}C (Table-2) while PS limit is 205^{o}C (Table-2) which is very high and must be improved. Lowering of 90 % point helps to reduce hydrocarbon contents and CO emissions and engine deposits during cold start and warm-up.

The gas chromatographic results, reveal the presence of C_{14} & C_{15} in all petrol samples which show that there is a mixing of some heavy fraction to earn more profit. This practice has bad impact on the petrol quality and on the environment.

Table-1. **Retention Times of Hydrocarbon Standards by Gas Chromatography**

Standard	Retention time (min.)	Standard	Retention time (min.)
(Saturates)			
Pentane	3.40	Hexane	3.43
Heptane	3.48	Nonane	3.63
Decane	3.89	$C_{14}H_{30}$	8.04
$C_{15}H_{32}$	9.50		
(Aromatics)			
Toluene	3.79	Benzene	4.1
Ethylbenzene	5.28	Xylene	5.34
Cumene	5.60	ter. Butyl benzene	6.34
Polars			
Pentanol	7.17	Alpha naphthol	6.99

Table 2. **Standard Specification of European, Indian and Pakistani Gasoline.**

Property	**European* Parliament 2005**	**AIAMCHARTER** 2005(Indian)**	**Pakistani Standard*** Specification**
Colour	-	Red (ULP)	Pinkish
Sp. Gravity 60/60^{o}F**** (max.)	-	-	0.76
Reid vapour Pressure (psi)@37.8^{o}F max.	50 kPa	-	10
Copper Strip Corrosion @ 50^{o}C max.	-	-	1a
Unleaded (%)	100	-	-
Distillation			
Initial Boiling Point (^{o}C)	-	-	Report
10% Recovery (^{o}C) max.	-	-	70
10-40 % Recovery (^{o}C) max.	-	70	-
46% Recovery (^{o}C) max	10	-	-
50% Recovery (^{o}C) max.	-	-	125
65%Recovery (^{o}C) max.	-	100	-
75% recovery (^{o}C) max.	100	-	-
90% Recovery (^{o}C) max.	-	180	180
Final Boiling Point (^{o}C) Max	-	195	205
Total Recovery (Vol %.)	-	-	Report
Residue (% v/v) Maximum	-	2.0	-
.Olefins (% v/v) max.	18	10	-
Aromatics (%v/v) max	42	35	-
Benzene (% v/v) max.	1.0	1.0	-
Oxygen (wt/wt %)	2-3	2-5	-
Sulphur (%wt/wt) max.	0.005	0.003	-

*Data reproduced from Cleaning the Air –Better Vehicle, Better Fuels; Published by Tata Energy Research Institute (TERI) India, p.245, 2002.
** Data Source. AIAM (1999) and BIS (1995 b), Clearing the Air –better Vehicle, better fuels; Published by Tata Energy Research Institute (TERI) India, p-231, (2003).
***STANDARD TEST LIMITS ARE PRODUCED FROM PAKISTAN STANDARD 1430:1999 (UDC: 665.733.5)
****Ministry of Petroleum & Natural Resources of has directed "to report" the Sp. Gravity at 60/60^{o}F.

Table-3. **Analytical Results of Physical Parameters and Hydrocarbon Contents in Gasoline of PSO**

Parameter	ASTM METHOD	S-1	S-2	S-3	S-4	Range	Mean	STDEV.
Colour		Pink	Pink	Pink	Pink	0.000-0.000	0.000	0.000
Sp. Gravity 60/60^{o}F	D-1298	0.761	0.754	0.767	0.761	0.751-0.767	0.761	0.005
Reid vapour Pressure								
(psi) @37.8^{o}F	D-323	9.800	9.600	9.500	9.700	9.500-9.800	9.650	0.129
Copper Strip Corrosion								
@ 50^{o}C	D-130	1a	1a	1a	1a	0.000-0.000	1a	0.000
Residue/Loss		1/1	1/1	1/1	1/1	0.000-0.000	1/1	0.000
Distillation	D-86							
I.B.P. (^{o}C)		45.00	42.00	42.00	42.00	42.00-45.00	42.75	1.500
10%Recovery (^{o}C)		58.00	58.00	58.00	58.00	0.000-0.000	58.00	0.000
50% Recovery (^{o}C)		98.00	95.00	100.0	98.00	95.00-100.0	97.75	2.061
90% Recovery (^{o}C)		145.0	142.0	148.0	145.0	142.0-148.0	145.0	2.450
F.B.P. (^{o}C)		185.0	182.0	190.0	185.0	182.0-190.0	184.0	3.317
Total Recovery (Vol %)		98.00	98.00	98.00	98.00	0.000-0.000	98.00	0.000
Pentane (wt %)		12.71	7.220	12.11	--	7.220-12.71	10.68	3.011
Hexane (wt %)		13.96	7.540	11.77	--	7.540-13.96	11.09	3.264
Heptane (wt %)		2.249	2.500	1.990	--	1.990-2.500	2.246	0.255
Octane (wt %)		2.247	3.220	2.970	--	2.247-3.220	2.812	0.505
Nonane (wt %)		0.000	1.630	1.530	--	1.530-1.630	1.580	0.071
Decane (wt %)		0.000	0.525	0.640	--	0.525-0.640	0.583	0.081
$C_{14}H_{30}$ (wt %)		2.741	2.555	1.911	--	1.911-2.741	2.402	0.436
$C_{15}H_{32}$ (wt %)		0.425	0.637	0.406	--	0.406-0.637	0.489	0.128
Toluene (wt %)		0.930	0.000	0.420	--	0.420-0.930	0.675	0.361
Benzene (wt %)		5.037	3.515	5.073	--	3.515-5.073	4.542	0.889
Ethylbenzene (wt %)		11.16	9.126	18.20	--	9.126-18.20	12.83	4.761
Xylene (wt %)		19.27	13.13	11.56	--	11.56-19.27	14.65	4.074
Cumene (wt %)		11.16	7.620	7.890	--	7.620-11.16	8.890	1.971
Ter.butylbenzene (wt %)		2.269	1.880	1.340	--	1.340-2.269	1.830	0.500
Alpha naphthol (wt %)		9.447	7.863	6.180	--	6.180-9.447	7.830	1.630
Total Saturates(wt %)		34.34	29.34	33.33	--	29.34-34.34	32.34	2.640
Total Aromatics (wt %)		49.83	35.27	44.48	--	35.27-49.83	43.19	7.360
Total Polars (wt %)		9.450	7.860	6.180	--	6.180-9.450	7.830	1.640

Table - 4. **Analytical Results of Physical Parameters and Hydrocarbon Contents in Gasoline of SHELL**

Parameter	**ASTM METHOD**	**S-1**	**S-2**	**S-3**	**S-4**	**Range**	**Mean**	**STDEV.**
Colour		Pink	Pink	Pink	Pink	0.000-0.000	Pink	0.000
Sp. Gravity 60/60^{o}F	D-1298	0.760	0.756	0.754	0.759	0.754-0.760	0.757	0.003
Reid vapour Pressure (psi) @37.8^{o}F	D-323	10.00	9.900	9.700	9.800	9.700-10.00	9.850	0.129
Copper Strip Corrosion @ 50^{o}C	D-130	1a	1a	1a	1a	0.000-0.000	1a	0.000
Residue/Loss		1/1	1/1	1/1	1/1	0.000-0.000	1/1	0.000
Distillation	D-86							
I.B.P. (^{o}C)		45.00	45.00	45.00	42.00	42.00-45.00	44.25	1.500
10%Recovery (^{o}C)		58.00	56.00	56.00	58.00	56.00-58.00	57.00	1.155
50% Recovery (^{o}C)		98.00	95.00	95.00	98.00	95.00-98.00	96.50	1.732
90% Recovery (^{o}C)		148.0	145.0	148.0	145.0	145.0-148.0	146.5	1.732
F.B.P. (^{o}C)		182.0	182.0	182.0	180.0	180.0-182.0	181.5	1.000
Total Recovery (Vol %)		98.00	98.00	98.00	98.00	0.000-0.000	98.00	0.00
Pentane (wt %)		3.910	8.020	18.93	13.92	3.910-19.92	11.21	6.585
Hexane (wt %)		11.25	15.28	22.70	14.97	11.25-22.70	16.05	4.797
Heptane (wt %)		2.250	7.520	7.500	7.000	2.250-7.520	6.068	2.556
Octane (wt %)		2.170	3.132	3.100	2.960	2.170-3.132	2.841	0.453
Nonane (wt %)		2.100	2.220	2.200	0.973	0.973-2.220	1.873	0.603
Decane (wt %)		0.250	0.092	0.092	0.109	0.092-0.250	0.136	0.077
$C_{14}H_{30}$ (wt %)		2.599	0.225	0.529	1.493	0.225-2.599	1.212	1.071
$C_{15}H_{32}$ (wt %)		0.376	0.229	0.595	0.238	0.229-0.595	0.360	0.171
Toluene (wt %)		1.707	0.101	0.000	0.139	0.101-1.707	0.649	0.916
Benzene (wt %)		4.950	6.640	5.257	4.930	4.930-6.640	5.444	0.811
Ethylbenzene (wt %)		5.600	7.030	6.600	10.00	5.600-10.00	7.308	1.892
Xylene (wt %)		32.15	11.00	17.30	9.650	9.650-32.15	17.53	10.30
Cumene (wt %)		11.38	11.38	11.19	4.480	4.480-11.38	9.608	3.420
Ter.butylbenzene (wt %)		2.280	1.320	3.040	1.260	1.260-3.040	1.975	0.850
Pentanol (wt %)		5.762	0.206	0.445	0.179	0.179-5.762	1.648	2.745
Alpha naphthol (wt %)		0.000	5.148	10.37	5.136	5.136-10.37	6.886	3.020
Total Saturates(wt %)		24.91	36.72	55.65	41.66	24.91-55.65	39.74	12.73
Total Aromatics (wt %)		58.07	37.47	43.39	30.46	30.46-58.07	42.35	11.74
Total Polars (wt %)		5.760	5.350	10.82	5.320	5.320-10.82	6.810	2.680

Table-5. **Analytical Results of Physical Parameters and Hydrocarbon Contents in Gasoline of CALTEX**

Parameter	ASTM METHOD	S-1	S-2	S-3	S-4	Range	Mean	STDEV.
Colour		Pink	Pink	Pink	Pink	0.000-0.000	Pink	0.000
Sp. Gravity 60/60^{o}F	D-1298	0.756	0.762	0.755	0.760	0.755-0.762	0.758	0.003
Reid vapour Pressure (psi) @37.8^{o}F	D-323	9.600	9.900	9.500	9.700	9.500-9.900	9.670	0.171
Copper Strip Corrosion @ 50^{o}C	D-130	1a	1a	1a	1a	0.000-0.000	1a	0.000
Residue/Loss		1/1	1/1	1/1	1/1	0.000-0.000	1/1	0.000
Distillation	D-86							
I.B.P. (^{o}C)		42.00	42.00	45.00	42.00	42.00-45.00	42.75	1.500
10%Recovery (^{o}C)		55.00	58.00	55.00	58.00	55.00-58.00	56.50	1.732
50% Recovery (^{o}C)		98.00	100.0	95.00	98.00	95.00-100.0	97.75	2.061
90% Recovery (^{o}C)		148.0	148.0	145.0	148.0	145.0-148.0	147.3	1.500
F.B.P. (^{o}C)		188.0	188.0	185.0	185.0	185.0-188.0	186.5	1.732
Total Recovery (Vol %)		98.00	98.00	98.00	98.00	0.000-0.000	98.00	0.000
Pentane (wt %)		13.88	14.28	15.80	15.16	13.88-15.80	14.78	0.865
Hexane (wt %)		8.710	30.82	14.70	9.180	8.710-30.82	15.86	10.34
Heptane (wt %)		6.860	7.240	8.020	2.310	2.310-8.020	6.108	2.577
Octane (wt %)		2.180	2.070	2.350	2.430	2.070-2.430	2.258	0.163
Nonane (wt %)		0.839	0.227	2.130	1.050	0.227-2.130	1.062	0.793
Decane (wt %)		0.357	0.113	0.256	0.289	0.113-0.357	0.254	0.103
$C_{14}H_{30}$ (wt %)		1.667	1.286	0.239	1.600	0.239-1.667	1.198	0.661
$C_{15}H_{32}$ (wt %)		0.306	0.196	0.000	0.175	0.175-0.306	0.226	0.070
Toluene (wt %)		0.263	0.125	0.238	0.263	0.125-0.263	0.222	0.066
Benzene (wt %)		4.724	3.890	4.853	7.540	3.890-7.540	5.252	1.584
Ethylbenzene (wt %)		8.271	9.722	9.882	9.630	8.271-9.882	9.376	0.744
Xylene (wt %)		10.90	9.720	9.342	12.70	9.342-12.70	10.67	1.510
Cumene (wt %)		0.431	6.050	6.890	7.870	0.431-7.870	5.310	3.337
Ter.butylbenzene (wt %)		5.104	1.132	1.040	1.340	1.04-5.1040	2.154	1.974
Pentanol (wt %)		0.233	0.166	0.280	0.172	0.166-0.233	0.213	0.054
Alpha naphthol (wt %)		0.000	4.684	5.370	5.753	4.684-5.753	5.269	0.542
Total Saturates(wt %)		34.80	56.23	43.50	32.19	32.19-56.23	41.68	10.84
Total Aromatics (wt %)		29.69	30.64	32.25	39.34	30.64-39.34	32.98	4.370
Total Polars (wt %)		0.023	4.850	5.650	5.930	0.230-5.930	4.170	2.660

Conclusion

The motor gasoline available in Multan region does not conform to the European or Indian standard specifications. These gasoline samples are according to the PS specification. We must improve its quality according to the international standards to save the environment.

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