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Fuel Design as Constructional Element with the Example of Biogenic and Fossil Diesel Fuels

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SUMMARY

Different fuels, in detail: three blends from methyl esters of rapeseed oil, soy bean oil, and palm oil; neat rapeseed oil methyl ester; a gas-to-liquid fuel (GTL); and two new diesel fuel qualities from Aral and Shell (Ultimate resp. V-Power) were compared to reference diesel fuel (DF) with focus on emissions.
Therefore, the regulated emissions carbon monoxide (CO), hydrocarbons (HC), nitrogen oxide (NO_x) and particulate matter (PM) and the non regulated particle size distribution were determined. Additionally to the emissions the mutagenic potency of conventional reference diesel fuel, biodiesel, Shell V-Power Diesel, and Aral Ultimate Diesel was tested.
In the result of all investigations it becomes clear that the potency of fuel systems engineering as constructional element should be considered for the joint development of biogenic and fossil fuels and engines.

KEYWORDS: *Biogenic fuels; Biodiesel; FAME; GTL; Diesel fuel; Emissions; Health effects*

1 SCOPE AND GOAL

Recently biodiesel (fatty acid methyl ester, FAME – in Germany mainly rapeseed oil methyl ester as a neat fuel, which means B100) became an important alternative fuel on the German and the European markets. Approximately 1,200,000 tons were sold in Germany in the year 2004 [1]. This is more than 50 % of all biodiesel that is sold in the European Union [2]. Today biodiesel is available at nearly 1,900 filling stations in Germany.

One driving-force for biofuels is the Directive 2003/30/EC of the European Parliament and of the Council [3] that shall push biofuels to a market share of 2 % in 2005 and up to 5.75 % in 2010, cf. also [4], [5]. Regarding the finiteness of fossil resources, the reduction of climate gas emissions, and the maintenance of rural structures this directive can be considered as noticeable contribution on the way to a future sustainable mobility.

However, the use of any liquid fuel in highly efficient internal combustion engines leads to NO_x emissions. Regarding biodiesel, these emissions are considerably higher versus fossil diesel fuel (DF) [6]. Due to that significant disadvantage of biodiesel, a biodiesel sensor was developed recently [7], [8]. The sensor discriminates neat biodiesel and its blends with DF and provides this blend signal to the engine management unit (EMU). The EMU controls the whole timing and dosage of the fuel injection. Thus it enables the reduction of nitrogen oxides (NO_x) to the level of DF by software means [9].

It was the goal of the research work reported here to reduce especially the NO_x emissions by the way of fuel design as alternative or complementary strategy to the biodiesel sensor. For these investigations FAME qualities from palm oil, soybean oil and rape seed oil were used.
As a close-by prototype of possible future Fischer-Tropsch fuel from biomass, a gas-to-liquid fuel (GTL) was tested. With the GTL no blending experiments were carried out.

As reference for all fuels reference DF (DIN EN 590) was chosen. All FAME qualities were within or at least quite close to the DIN EN 14214 specification.
Another goal was the comparison of new diesel fuels, such as Aral Ultimate Diesel and Shell V-Power Diesel, with conventional diesel fuel and biodiesel.

2 ENGINE AND FUELS

The test engine was a six-cylinder, 205 kW Mercedes-Benz OM 906 that meets the exhaust gas standard according to Euro III. Table 1 presents some of the engine characteristics.

Table 1: Engine description

Stroke of cylinder	130 mm
Bore of cylinder	102 mm
Number of cylinders	6
Stroke volume	6370 cm^3
Normal rate of revolutions	2300 min^{-1}
Rated power	205 kW
Maximum torque	1100 Nm @ 1300 min^{-1}
Compression ratio	17.4

On the engine test bench the 13-mode ESC test was run, using an eddy-current break. The sampling of regulated gaseous compounds was taken from the pure exhaust gas stream. For particulate matter a dilution tunnel was used. As filter material PTFE-coated filters T60A20 (Pall) were chosen. The sampling time was constant, whereas the sampling volumetric flow rate was adapted to the dilution and the weighting factors. For all fuels at least a two-times repeated determination of emissions was carried out.

Different FAME qualities were blended from rape seed, palm and soybean oil. Neat RME was according to DIN EN 14214. Soybean oil methyl ester (with higher iodine number as RME) and palm oil methyl ester (with shorter chain lengths as RME) were blended with RME. With the exception of the oxidation stability for FAME 1 and FAME 4, all biogenic fuels met the DIN EN 14214, as shown in table 2. The properties of the different biogenic fuels may be compared to other qualities available on the international markets by using data from a recently published handbook [10]. The data for reference DF, GTL, Aral Ultimate Diesel, and Shell V-Power Diesel are given in table 3. GTL was provided by the Volkswagen AG.

For the determination of the mutagenic potency other fuels were used. Their analyses are not reported in this paper.

Table 2: Properties of all FAME qualities and limits according to DIN EN 14214

Property	Result				Unit	Limits	
	FAME 1	FAME 2	FAME 3	FAME 4		Min.	Max.
rapeseed oil methyl ester	75	100	45	60	vol. %		
soybean oil methyl ester	25	0	0	12.5	vol. %		
palm oil methyl ester	0	0	55	27.5	vol. %		
density (15 °C)	0.8836	0.8832	0.8789	0.8818	g/mL	0.86	0.900
kin. viscosity (40 °C)	4.345	4.333	4.516	4.459	mm²/s	3.5	5.0
flashpoint	> 171	> 171	> 171	> 171	°C	120	
C.F.P.P.	-10	-15	-2	-6	°C		0/-20
water content	283	170	214	381	mg/kg		500
particulate content	4	2	3	1	mg/kg		24
oxidation stability	4.73	8.37	8.00	1.35	h	6	
neutralisation number	0.132	0.132	0.480	0.28	mg KOH/g		0.5
monoglycerides	0.46	0.61	0.25	0.34	wt. %		0.8
diglycerides	0.07	0.09	0.04	0.07	wt. %		0.2
triglycerides	< 0.01	< 0.01	< 0.01	< 0.005	wt. %		0.2
free glycerol	< 0.005	< 0.005	< 0.005	< 0.01	wt. %		0.02
total glycerol	0.13	0.17	0.07	0.11	wt. %		0.25
iodine number	117	112	82	100	-		120
phosphorous content	< 1	< 1	< 1	< 1	mg/kg		10
alkali content	< 1	< 1	< 1	< 1	mg/kg		5
soap content	< 5	7	< 5	< 5	mg/kg		
earth alkali content	< 1	< 1	< 1	< 1	mg/kg		5
ester content	99.3	99.0	99.8	97.7	wt. %	96.5	

Table 3: Properties of DF, GTL, Aral Ultimate diesel fuel, and Shell V-Power diesel fuel as well as the limits according to DIN EN 590

Property	Result				Unit	Limit	
	DF	GTL	Ultimate	V-Power		Min.	Max.
density (15 °C)	0.8345	0.7868	0.8324	0.8326	g/mL	0.820	0.845
kin. viscosity (40 °C)	3.474	3.6	3.837	3.168	mm²/s	2.0	4.5
flashpoint	100	126	101	70	°C	55	
C.F.P.P.	-20	+3	-9	-19	°C		0/-20[1)]
water content	30	48	24	65	mg/kg		200
particulate content		7	1	23	mg/kg		24
oxidation stability	1	2.2 h[2)]	0.3	2.9	g/m^3		25
neutralisation number	0.0	0.039			mg KOH/g		
sulfur content	35	<2	1.0	5,9	mg/kg		350
carbon residiue	<0.01	0.03	<0.01	0.05	wt. %		0.3
cetan number	53.4	79	<60.5	60.5	-	51.0	
HFRR	426		351	331	µm		460
monoaromatics	16.4				vol. %		
diaromatics	3.4				vol. %		
polyaromatics	0.01		0.9	2.4	vol. %		

[1)]summer/winter quality [2)]according to EN 14112

3 RESULTS

The comparison of biodiesel (FAME 2) and fossil diesel fuels follows the well known tendencies. For biodiesel, carbon monoxide (CO), hydrocarbons (HC), and particulate matter (PM) emissions are reduced, whereas NO_x emissions increase.

Regarding all fuels it can be summarized that CO emissions are always below the Euro III limit of 2.1 g/kWh (figure 1). It becomes obvious that FAME reduces CO versus DF to 60 %, whereas GTL, Ultimate Diesel, and V-Power Diesel lead to an increase; in maximum to approx. 120 %. There is no significant difference between the four FAME qualities.

In figure 2 the results of the HC measurements are presented. All FAME qualities emit approximately 30 % less HC than DF. FAME 1 and 3 express slightly better results than 2 and 4. GTL is in between of FAME and DF. The results of Ultimate Diesel and V-Power Diesel are in between DF and GTL. All fuels meet the Euro III limit of 0.66 g/kWh for HC.

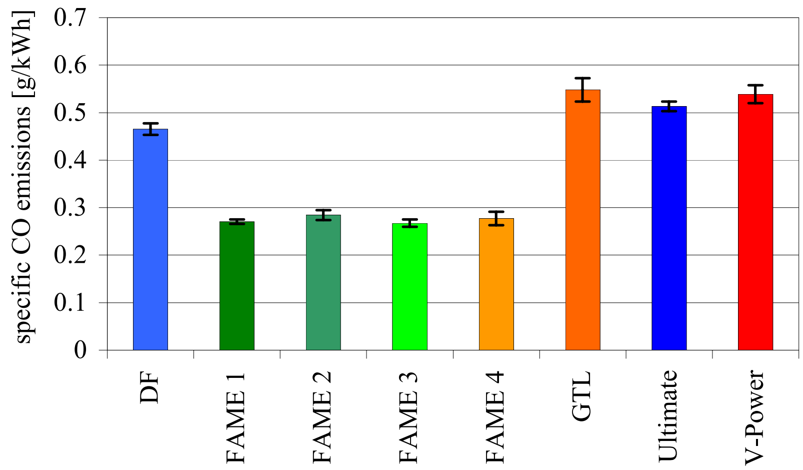

Figure 1: Specific CO emissions for different fuels; 13-mode ESC test

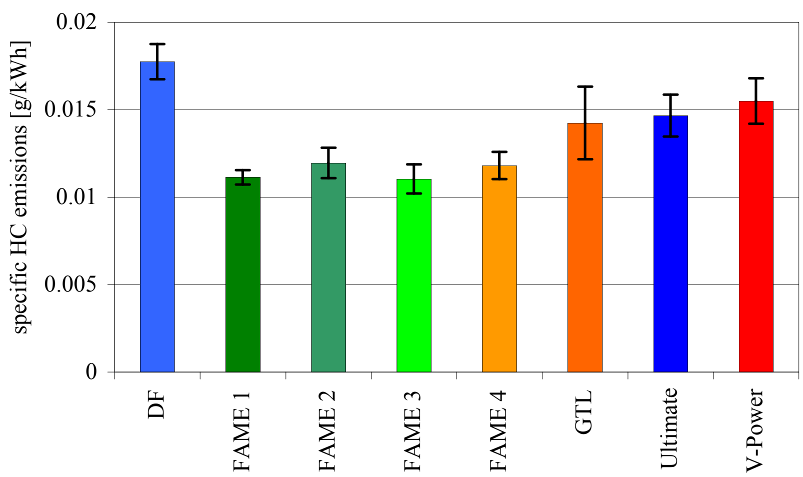

Figure 2: Specific HC emissions for different fuels; 13-mode ESC test

Regarding PM emissions DF leads to the highest value – however, with the most extended error bar of all PM measurements; cf. figure 3. GTL is approximately 20 % better than DF, and the results of all FAME qualities are significantly below GTL and the new diesel fuels. In contrast to the findings with respect to CO and HC the FAME results here noticeably differ from each other. For example, FAME 2 emits 70 % more than FAME 4. In all FAME 2 leads to the worst result of all FAME qualities.
GTL, Ultimate Diesel, and V-Power Diesel prove to be better than DF but worse than all FAME qualities. None of the fuels exceeds the Euro III limit of 0.1 g/kWh.

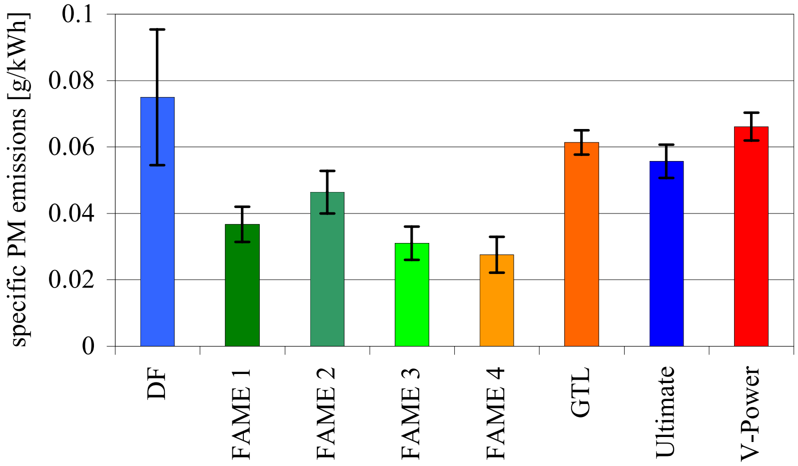

Figure 3: Specific PM emissions for different fuels; 13-mode ESC test

In addition to the gravimetric value the particle number distribution – as non-regulated emission – was determined by a scanning mobility particle sizer (SMPS; from TSI) and an electronic low pressure impactor (ELPI; from Dekati). The physical operation principles of these analysers are given in [11]. Data for Ultimate Diesel and V-Power Diesel were not available for this paper.

As expected, particle sizes below 1 µm dominated. Therefore larger diameters were not taken into account. The ELPI results reveal that the two smallest classes (28 to 55 nm and 55 to 94 nm) emit most, whereas a logarithmic decrease becomes obvious for the larger classes; cf. figure 4. The FAME qualities do not differ significantly from each other. But a strong advantage of all FAME qualities towards DF and GTL must be considered that are both fairly comparable. The latter is in contrast to the gravimetric PM values reported previously (cf. figure 3), where DF and GTL differ.

SMPS results are similar to ELPI in the range above 40 nm; see figure 5. However, GTL emits a few less than DF. Below 30 nm the particle numbers of the fossil fuels decrease, whereas the biofuels lead to a 10-fold increase. The qualities 1, 2, and 3 are quite comparable. Only FAME 4 differs significantly from the others.

Both the results form ELPI and SMPS are reproducible. However, at present it is not possible to give a concluding assessment for the ultra-fine particle results. Future investigations concerning the composition of the ultra-fine particles must solve the question whether they consist of soot or unburned fuel.

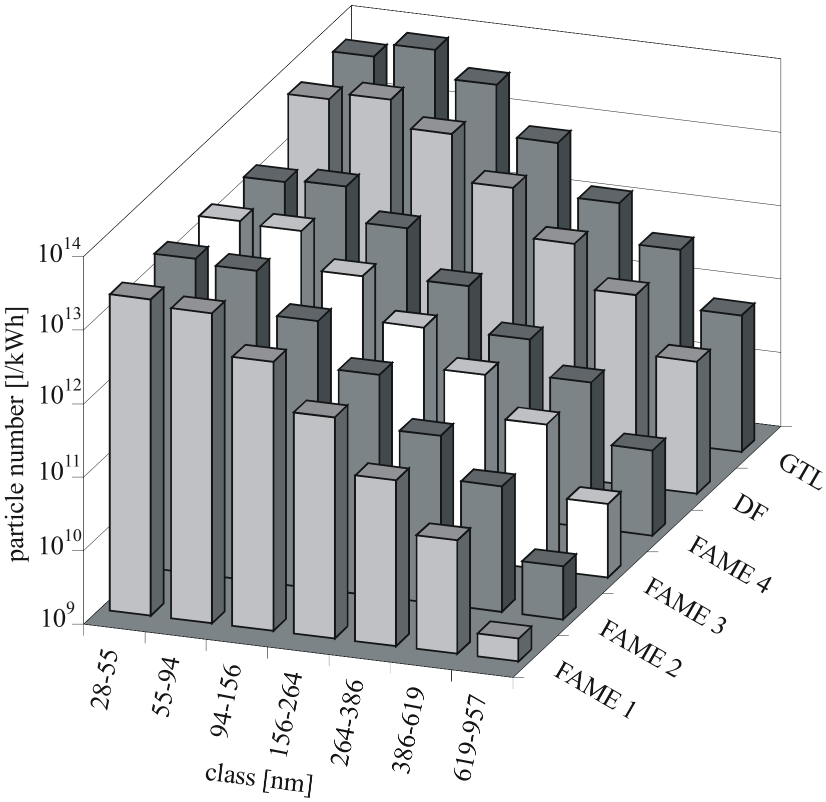

Figure 4: Particle number distributions for different fuels by ELPI; 13-mode ESC test

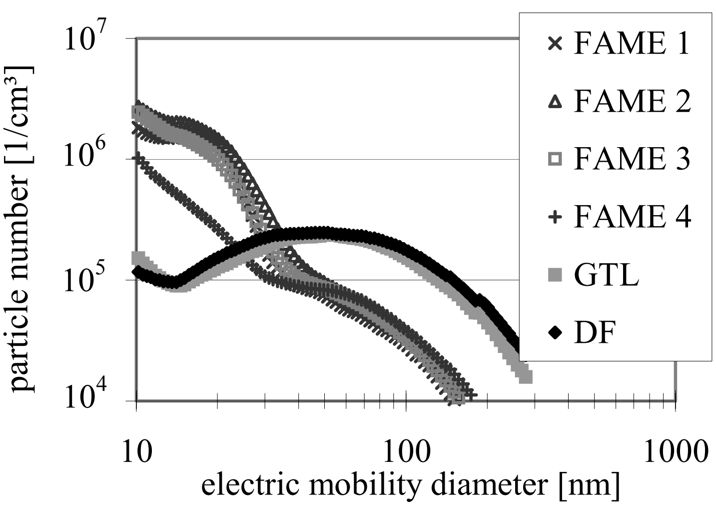

Figure 5: Particle number distributions for different fuels by SMPS; 13-mode ESC test

For mutagenicity assays performed at the University of Göttingen, diesel engine particles (DEP) were sampled on PTFE-coated glass fibre filters (T60A20, from Pallflex Products Corp.) when the engine was fuelled with DF, V-Power Diesel, Ultimate Diesel, and RME. After gravimetrical determination of the particle masses the filters were extracted with dichloromethane in a soxhlet apparatus [12], and weighed again to determine the soluble fraction of the sampled DEP. The extracts were reduced by rotary evaporation, dried under a stream of nitrogen, and redissolved in 4 ml dimethyl sulfoxide (DMSO).

Extracts were tested for mutagenicity in the *Salmonella typhimurium* / mammalian microsome assay [13] using the revised standard test protocol with the tester strain TA98 [14]. The test system detects mutagenic properties of a wide spectrum of chemicals and is adopted as an OECD-method (guideline No. 471). The Ames test is the most frequently used assay in order to investigate mutagenicity of complex mixtures like combustion products. TA98 is most sensitive for the detection of mutagens in organic extracts of DEP that cause frameshift mutations. As a surrogate of the liver-metabolism in humans (mammals) the tests were performed with (+S9) and without (-S9) metabolic activation by microsomal mixed-function oxidase systems from livers of young male Wistar rats [14]. This assay was already successfully used in previous investigations of our study group [15, 16].

The fuels Ultimate Diesel and RME showed less than 50% mutagenic effects in tester strain TA98 compared with DF; cf. figure 6. The lowest genotoxicity was observed for RME. When the engine was fuelled with V-Power Diesel, the mutagenicity was reduced by 40 %. The mutagenic response was decreased further in each of the four fuels by adding a metabolic activation system (S9).

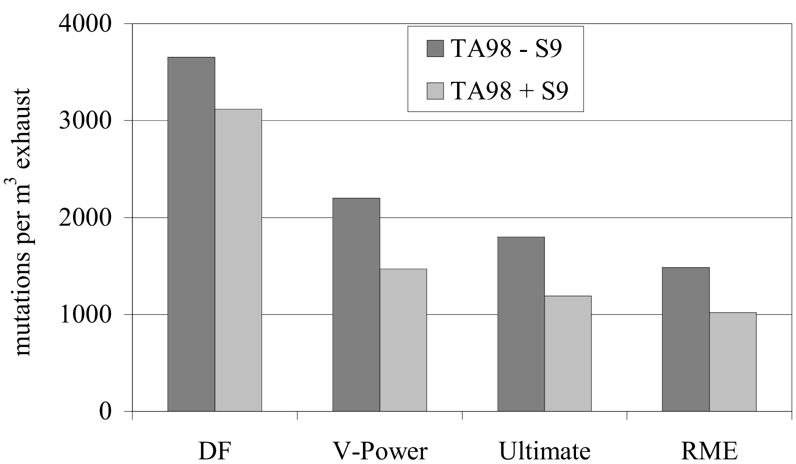

Figure 6: Mutagenicity of particle extracts of four fuels in the tester strain TA98 ;13-mode ESC test

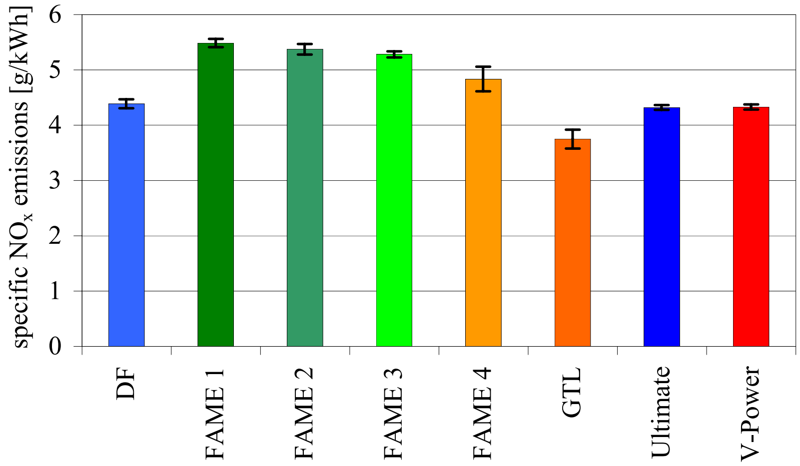

Figure 7: Specific NO_x emissions for different fuels, 13-mode ESC-test

These results add further evidence that genotoxic and obviously also carcinogenic effects of diesel engine particles can successfully be reduced by an optimisation of the fuel composition.

The results for NO_x emissions are presented in figure 7. The Euro III limit of 5 g/kWh is only obeyed by DF, GTL, Ultimate Diesel, V-Power Diesel, and almost by FAME 4. The other fuels exceed the limit. Currently it cannot be explained why FAME 4 shows reproducibly better results than the other FAME qualities. This question is part of future investigations. Today the advantage of FAME 4 can only be demonstrated, but unfortunately not yet be explained.

In summary, regarding these NO_x results it becomes obvious that a modified biodiesel can meet the exhaust gas regulations. So the potency of systematic fuel research seems to be a great chance for both engine and fuel development – in case it is carried out jointly.

4 CONCLUSIONS

Different fuels, in detail: three blends from methyl esters of rapeseed oil, soy bean oil, and palm oil; neat rapeseed oil methyl ester; a gas-to-liquid fuel (GTL); and two new diesel fuel qualities from Aral and Shell (Ultimate resp. V-Power) were compared to reference diesel fuel (DF) with focus on emissions.

With respect to CO and HC, none of the fuels exceeded the regular limits. All biodiesel blends led to better emissions than the diesel fuels and GTL.

All fossil diesel fuels and GTL fulfilled the NO_x and PM limit values. GTL showed best NO_x results of all fuels. The use of all biodiesel qualities resulted in PM reduction and NO_x increase. Only one biodiesel met just about the NO_x limit. However, the four biodiesel qualities differed noticeably in PM and NO_x.

With the exception of CO, GTL always led to better results of regulated emissions than conventional diesel fuel (DF). Except for NO_x biodiesel emitted less regulated compounds than GTL and all diesel fuels. Concerning NO_x emissions, the potency of biogenic fuel seems to be not yet exploited sufficiently.

Additionally to the emissions, the mutagenic potency of conventional reference diesel fuel, biodiesel, Shell V-Power Diesel and Aral Ultimate Diesel was determined. In the result biodiesel showed the lowest mutagenicity. However, the new diesel fuels from Aral and Shell demonstrate that fossil diesel fuels are on their way to be improved regarding their health effects. In detail, Aral Ultimate Diesel reaches nearly the good biodiesel result.

As a result of all investigations it becomes clear that the potency of fuel systems engineering as constructional element should be considered for the joint development of both engines and biogenic as well as fossil fuels.

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