14th ETH-Conference on Combustion Generated Nanoparticles
August 1st – 4th 2010

On the effects of a fuel-born DPF regeneration catalyst on vegetable oil used as a diesel engine fuel

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Background

Non-esterified vegetable oils are emerging as a popular fuel for diesel engines worldwide. Relatively high viscosity of vegetable oils, along with relatively high boiling points, often lead to deteriorated combustion and increased emissions of particulate matter at idle and low rpm and loads. Along with low exhaust gas temperatures at low rpm and loads, such characteristics may pose a challenge for diesel particulate filters (DPF). On the other hand, previous tests *[Vojtisek-Lom, ETH 2009]* have shown that the PM generated at such conditions is mostly organic carbon, which „regenerates" at lower temperatures (250-300 ºC) compared to rest of the deposited particles (400-420 ºC, both on passive DPF with fuel-born iron-based catalyst). The question of DPF peformance with vegetable oils at low loads is still open. At medium and higher loads, PM emissions are lower and with higher organic fraction on rapeseed oil compared to diesel fuel. Good DPF operation with vegetable oil at high loads in co-generation units was also observed in *[Czerwinski et al, SAE 2008-01-1382]* and *[Soltic et al, Fuel, vol. 88, 2009, 1-8]* . Of concern is the effect of fuel-born catalysts. Presence of metals is one of the factors accelerating degradation of vegetable oils, worsening an already problematic long-term stability of these fuels.

Goal

To evaluate the effect of the presence of a fuel-born catalyst in non-esterified rapeseed oil on long-term stability and degradation of the fuel, and on diesel particulate trap regeneration (ability to regenerate, balance point temperature, regeneration rate) on a turbodiesel engine fueled by heated fuel-grade rapeseed oil.

Experimental

A Zetor 1505 turbodiesel tractor engine (525 Nm @ 1480 rpm, 90 kW @ 2200 rpm) was tested in the departmental laboratory on a Schenck Dynabar D-630 water brake dynamometer. The engine was powered alternately by diesel fuel and by heated fuel-grade rapeseed oil (FabioProduct, Holín, Czech Republic). The engine was fitted with a non-catalyzed DPF (HUSS Umwelttechnik). A fuel-borne catalyst (FBC) (Satacene, Innospec) was added to the fuel at 0.1% by mass, or, at 5% Fe content, at 50 ppm Fe in fuel. Long term accumulation of mass determined by weighing the DPF after each test series. At the end, the DPF was fully regenerated, cleaned, and removed material was analyzed by X-ray fluorescence (XRF).

100 ml samples of a single batch of fuel-grade rapeseed oil without an additive and with 0.1% Satacene were aged for six months (a) in the sunlight (samples were stolen after about five months), (b) in an indoor dark cabinet, and (c) in a fuel storage shed outside. Portion of the last set was then heated to 90 ºC for 20 hours to simulate high-temperature environment in the vehicle fueling system. The concent of polymerized triacylglyceroles was determined by gel-permeation HPLC.

Results and discussion

The increase in DPF mass after combustion of approximately 300 kg of rapeseed oil and 200 kg of diesel fuel with 0.1% by weight Satacene added to the fuel (50 ppm Fe in fuel by weight) was approximately 30 g, subject to moisture fluctuations, which corresponds to 25 g Fe in FBC. X-ray fluorescence analysis of the particles removed from DPF has determined a metal content of 79.4% metals, of these: 91.1% Fe, 2.8% Zn, 2.1% Ca, 1.7% S, 1.1% P, 0.5% Si, 0.1% Na, Mg, Al, K, 0.3% other. Assuming that Fe is in the form of FeO, 72.3% (79.4% * 91.1%) of Fe corresponds to 20.7% of oxygen, which is in agreement with 20.6% non-metallic content of the material.

The HPLC measurements show no difference in polymer content of the fuels aged at ambient temperatures (0.12-0.15%), and show a marked increase due to heating of the fuel (3.98-4.07%, ~30x compared to values prior to heating, or 4-5x compared to non-additivated fuel, 0.89-0.94%).

Qualitative observations reveal that rapeseed oil with Satacene degraded faster, as denoted by darker color, characteristic odor, intensity of odor, and presence of polymerized semi-solids: After 2-3 months of not testing, rapeseed oil left in the auxiliary fueling system developed a darker color and smell characteristic for drying paint oil (linseed, …) – this smell is a sign of degradation (formation of oligomers with high molecular weight). After approx. 9 months of storage, rapeseed oil developed a darker color, and semi-solid, slimy chunks of polymerized oil settled in the fuel storage container (polyethylene) were captured on a strainer during refueling. These problems were not noticed with non-additivated rapeseed oil.

Degradation of vegetable oils proceeds slowly until antioxidants are depleted, then accelerates exponentially, with degradation products further accelerating the process *[Knothe, Fuel Processing Technology 88, 2007, 669-677]*. Returning heated fuel to the tank appears to contribute to the problem, and can be avoided by looping the fuel return, however, some heating of the tank is necessary in cold climates to keep the fuel liquid. <u>It is possible that similar problems may be expected with biodiesel which is more commonly used than vegetable oil!</u>

Conclusions

The DPF appears to regenerate fully with operation on heated fuel-grade rapeseed oil, with accumulated material in the DPF corresponding to non-combustible compounds from the fuel-born catalyst, engine lubricating oil, and wear particles.

The presence of an iron-based fuel-born catalyst (0.1% Satacene, 50 ppm Fe in fuel) in the rapeseed oil has resulted in accelerated degradation of the rapeseed oil, characterized by increased polymer content of the oil which was both measured and inferred from visual and olfactory indicators. It is possible that similar problems may be encoutered with using FBC with biodiesel.

Acknowledgements

The tests were funded by the Czech science foundation project 101/08/1717, Optimization of combustion of vegetable oils in diesel engines. The engine was loaned by the Tractor Research Institute (Zetor Brno, Czech Republic). The filter was loaned by Dr.-Ing. Hans-Jörg Rembor, HUSS Umwelttechnik, Germany. Thanks for the XRF analysis are given to Jaroslav Černý and Pavel Šimáček of the Department of Petroleum Technology and Alternative Fuels Institute of Chemical Technology, Prague.

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Background

- Non-esterified vegetable oils are emerging as a popular fuel for diesel engines worldwide.
- Relatively high viscosity of vegetable oils, along with relatively high boiling points, often lead to deteriorated combustion and increased emissions of particulate matter at idle and low rpm and loads.
- Along with low exhaust gas temperatures at low rpm and loads, such characteristics may pose a challenge for diesel particulate filters (DPF).
- On the other hand, previous tests *[Vojtisek-Lom, ETH 2009]* have shown that the PM generated at such conditions is mostly organic carbon, which „regenerates" at lower temperatures (250-300 ºC) compared to rest of the deposited particles (400-420 ºC, both on passive DPF with fuel-born iron-based catalyst). The question of DPF peformance with vegetable oils at low loads is still open.
- At medium and higher loads, PM emissions are lower and with higher organic fraction on rapeseed oil compared to diesel fuel. Good DPF operation with vegetable oil at high loads in co-generation units was also observed in *[Czerwinski et al, SAE 2008-01-1382]* and *[Soltic et al, Fuel, vol. 88, 2009, 1-8]*.
- Of concern is the effect of fuel-born catalysts. Presence of metals is one of the factors accelerating degradation of vegetable oils, worsening an already problematic long-term stability of these fuels.

Goal

To evaluate the effect of the presence of a fuel-born catalyst in non-esterified rapeseed oil on long-term stability and degradation of the fuel, and on diesel particulate trap regeneration (ability to regenerate, balance point temperature, regeneration rate) on a turbodiesel engine fueled by heated fuel-grade rapeseed oil.

Experimental – regeneration of DPF

- A Zetor 1505 turbodiesel tractor engine (525 Nm @ 1480 rpm, 90 kW @ 2200 rpm) was tested in the departmental laboratory on a Schenck Dynabar D-630 water brake dynamometer.
- The engine was powered alternately by diesel fuel and by heated fuel-grade rapeseed oil (FabioProduct, Holín, Czech Republic).
- The engine was fitted with a non-catalyzed DPF (HUSS Umwelttechnik). A fuel-borne catalyst (FBC) (Satacene, Innospec) was added to the fuel at 0.1% by mass, or, at 5% Fe content, at 50 ppm Fe in fuel.
- Long term accumulation of mass determined by weighing the DPF after each test series. At the end, the DPF was fully regenerated, cleaned, and removed material was analyzed by X-ray fluorescence (XRF).

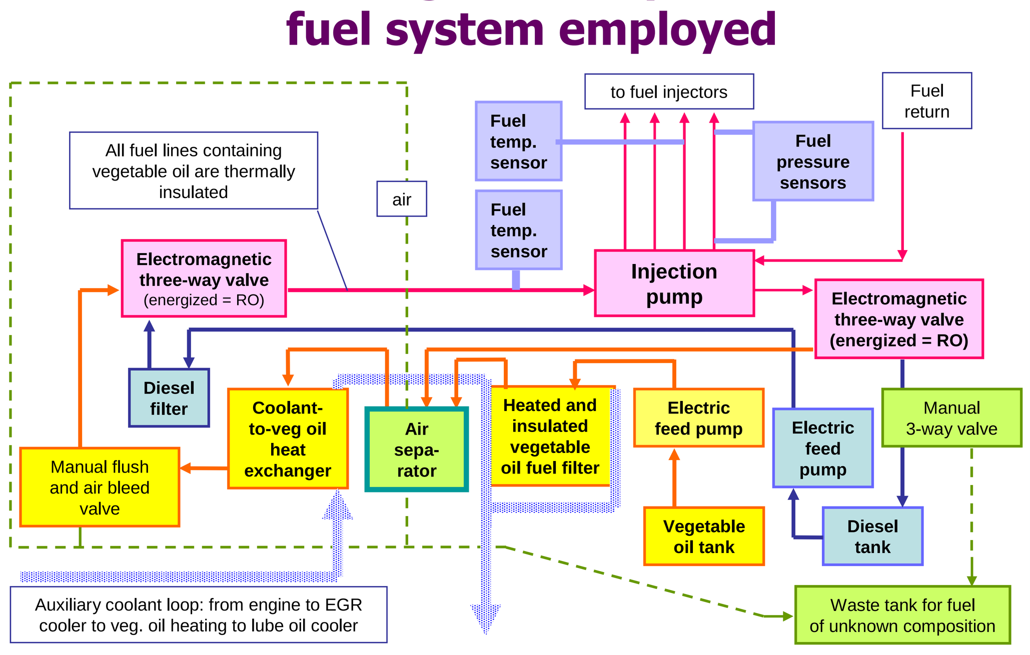
Experimental – stability of fuel

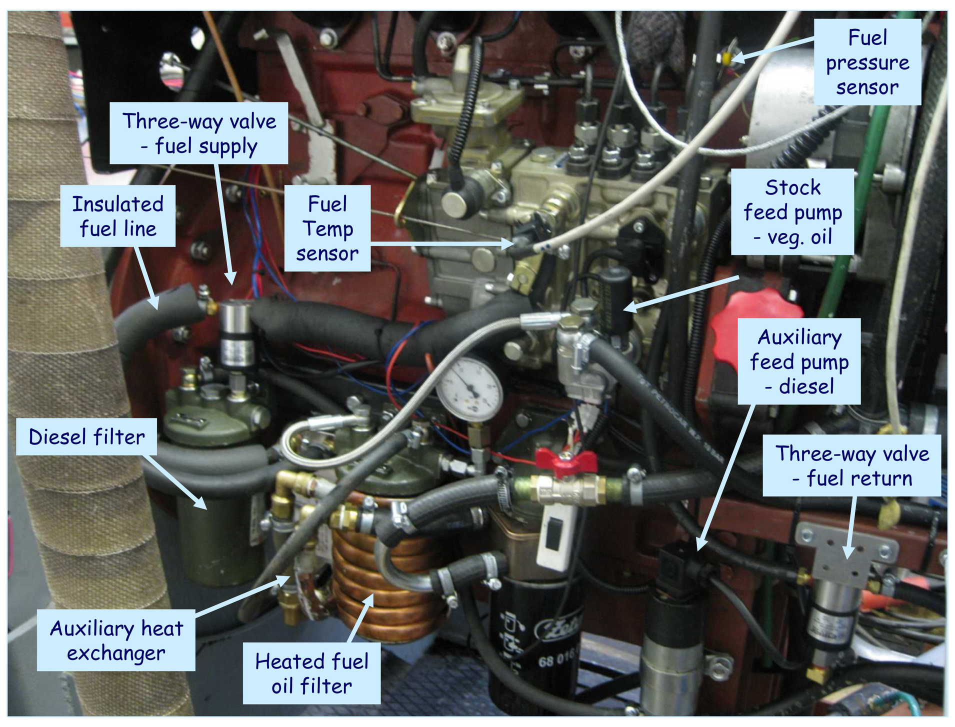
- 100 ml samples of a single batch of fuel-grade rapeseed oil without an additive and with 0.1% Satacene were aged for six months (a) in the sunlight (samples were stolen after about five months), (b) in an indoor dark cabinet, and (c) in a fuel storage shed outside.
- Portion of the last set was then heated to 90 ºC for 20 hours to simulate high-temperature environment in the vehicle fueling system.
- The concent of polymerized triacylglyceroles was determined by gel-permeation HPLC.

Discussion

- Long-term accumulation of the mass in DPF, ~30 g, generally corresponds to approximately 500 g of Satacene (25 g Fe) used.
- XRF analysis of the mass removed from DPF after regeneration reveals that metals account for 79.4% of material, of these, 91.1% is Fe from FBC, rest is believed to be from lubricating oil, engine wear, and ambient mineral dust.
- Assuming that Fe is in the form of FeO, 72.3% (79.4% * 91.1%) of Fe corresponds to 20.7% of oxygen, which is in agreement with 20.6% non-metallic content of the material.
- The HPLC measurements show no difference in polymer content of the fuels aged at ambient temperatures, and show a marked increase due to heating of the fuel (~30x compared to values prior to heating, or 4-5x compared to non-additivated fuel).
- Qualitative observations reveal that rapeseed oil with Satacene degraded faster, as denoted by darker color, characteristic odor, intensity of odor, and presence of polymerized semi-solids.
- Degradation of vegetable oils proceeds slowly until antioxidants are depleted, then accelerates exponentially, with degradation products further accelerating the process *[Knothe, Fuel Processing Technology 88, 2007, 669-677]*.
- Returning heated fuel to the tank appears to contribute to the problem, and can be avoided by looping the fuel return, however, some heating of the tank is necessary in cold climates to keep the fuel liquid.
- Similar problems may be expected with biodiesel which is more commonly used than vegetable oil!

Schematic diagram and photo of dual-fuel system employed

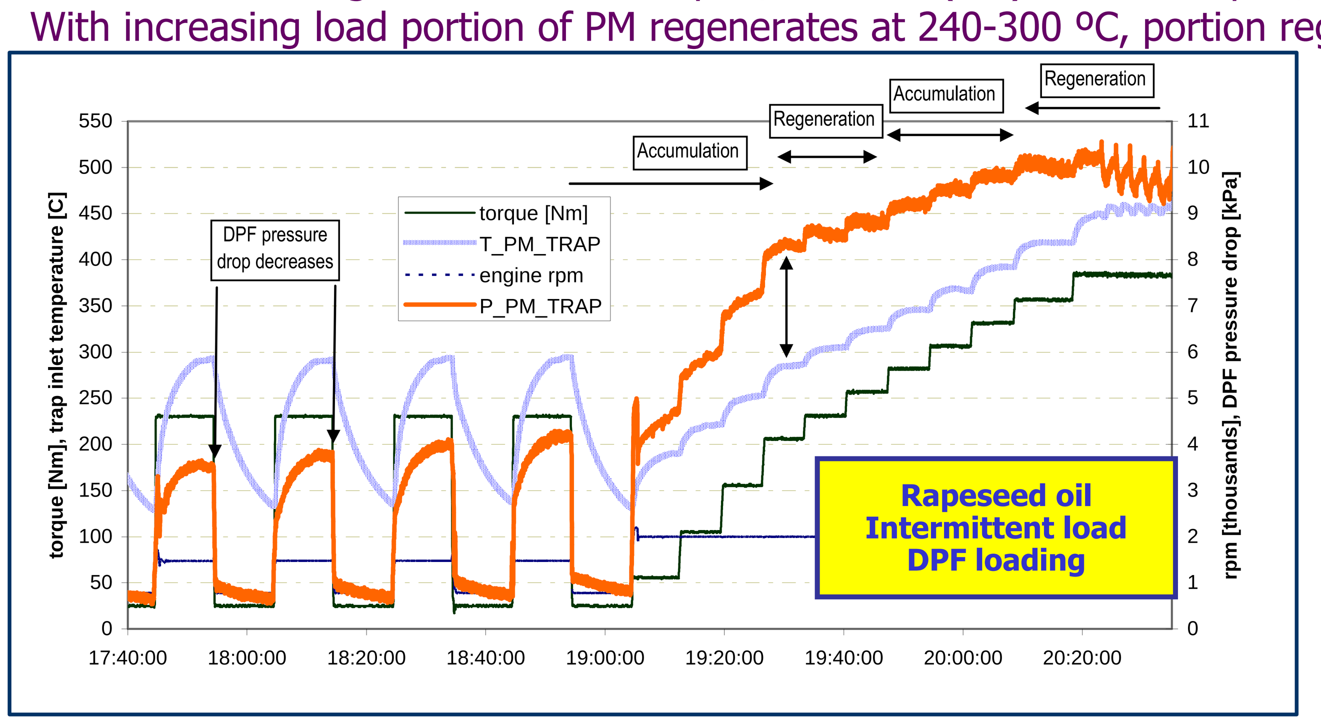


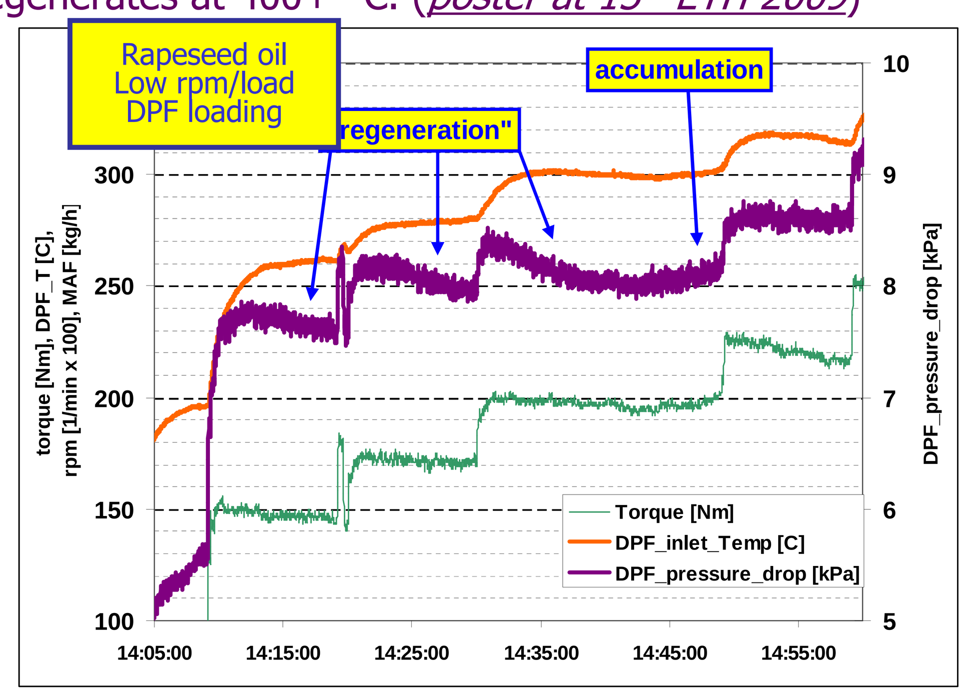


Heated rapeseed oil – DPF regeneration after loading of the filter at low rpm and loads

DPF loading at idle and 1480 rpm / 225 Nm (left) and 1240 rpm / 50 Nm (right), regeneration at 2000 rpm

With increasing load portion of PM regenerates at 240-300 ºC, portion regenerates at 400+ ºC. (*poster at 13th ETH 2009*)





Conclusions

- **The DPF appears to regenerate fully with operation on heated fuel-grade rapeseed oil, with accumulated material in the DPF corresponding to non-combustible compounds from the fuel-born catalyst, engine lubricating oil, and wear particles.**
- **The presence of an iron-based fuel-born catalyst (0.1% Satacene, 50 ppm Fe in fuel) in the rapeseed oil has resulted in accelerated degradation of the rapeseed oil, characterized by increased polymer content of the oil which was both measured and inferred from visual and olfactory indicators. It is possible that similar problems may be encoutered with using FBC with biodiesel.**

Results

Operation with DPF with FBC (Satacene): ~300 kg of rapeseed oil, ~200 kg of diesel, ~0.5 kg of Satacene (0.1% w/w)

Solid particles removed from DPF after ~500 ml of Satacene consumed with fuel

Increase in DPF mass: ~30 g
(subject to moisture fluctuations)
-Corresponds to ~25 g Fe
(Satacene contains 5% w/w Fe)

X-ray fluorescence analysis of the particles removed from DPF:
79.4% metals, of these:
91.1% Fe, 2.8% Zn
2.1% Ca, 1.7% S, 1.1% P,
0.5% Si, 0.1% Na, Mg, Al, K
0.3% other

79.4% of metals (20.6% of oxygen?) corresponds to 77.7% Fe by wt. in FeO, ***(79.4%*91.1%) Fe ~20.7% O2***

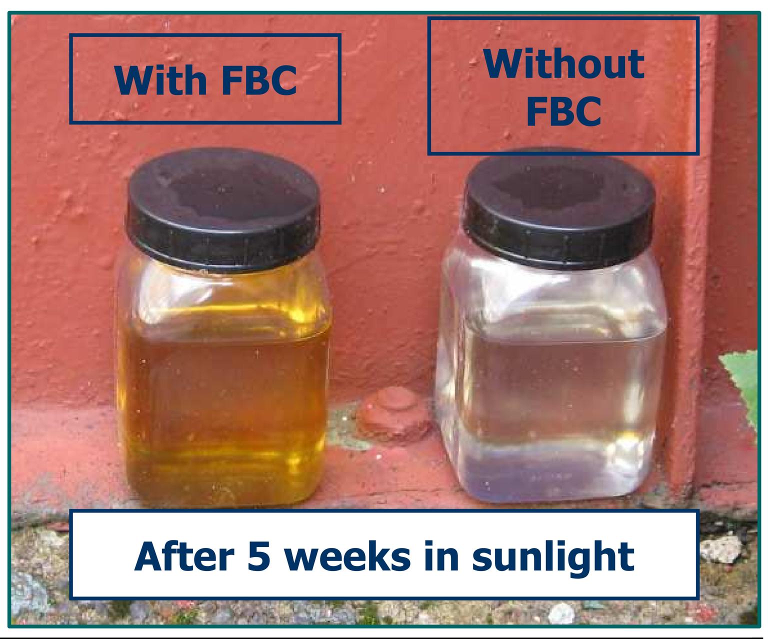
Aging of fuel-grade rapeseed oil with and without fuel born catalyst - 0.1% Satacene (50 ppm Fe)
Analysis of polymer triacylglycerol (TAG) content by HPLC

Aging in direct sunlight (samples stolen after 5 months)

Aging in dark cabinet

Aging in fuel shed

Heating (simulating circulation in the vehicle fuel system)



POLYMER CONTENT (HPLC)	Fuel-grade rapeseed oil no additives	Rapeseed oil + 0.1% Satacene (50 ppm Fe)
After 6 months aging in dark	**0.12-0.15%**	**0.12-0.15%**
After 6 months aging in indirect light (fuel shed)	**0.12-0.15%**	**0.12-0.15%**
After 6 months in fuel shed AND 20 hours at 90ºC	**0.86-0.94%**	**3.98-4.07%**

Experience with rapeseed oil with 0.1% Satacene:

After 2-3 months of not testing, rapeseed oil left in the auxiliary fueling system developed a darker color and smell characteristic for drying paint oil (linseed, …) – this smell is a sign of degradation (formation of oligomers with high molecular weight)

After approx. 9 months of storage, rapeseed oil developed a darker color, and semi-solid, slimy chunks of polymerized oil settled in the fuel storage container (polyethylene) were captured on a strainer during refueling.

These problems were not noticed with non-additivated rapeseed oil.

Polymerized rapeseed oil captured on a strainer during refueling – rapeseed oil with 0.1% Satacene by weight (50 ppm Fe) aged 9 months

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