Investigation of Gelled JP-8 and RP-1 Fuels

Richard Arnold*, Paulo H. S. Santos†, Travis Kubal‡,
Osvaldo Campanella§, William E. Anderson¶

Abstract—**For future airbreathing and rocket propulsion systems gelled propellants can be a promising replacement for conventional propellants. Especially for rocket engines, the application of a gelled fuel and gelled oxidizer can combine the advantages of conventional solid and liquid propellants without taking into account the specific disadvantages of both individual systems. The present publication describes the rheological behavior of gelled JP-8 turbine fuel and gelled rocket propellant RP-1, whereas fumed silica as a gelling agent has been used. Alongside the determination of an optimal mixing process, the rheological parameters of the investigated gelled hydrocarbon fuels showed a significant influence of the added amount of silica in comparison to the ungelled pure liquids.**

Keywords: ***hydrocarbon, JP-8, RP-1, gel, non-Newtonian, silica, advanced propellants, rocket engine***

1 Introduction

In general, gels are time-dependent, non-Newtonian fluids which have an almost solid like behavior when no shear stress is applied, and consist at least of the original fluid and the added gelling agent. During the gel mixing process, molecular forces like hydrogen bondings or van der Waals forces create a more or less soft solid structure, depending amongst others on the type and amount of added gelling agent.

Since the requirements for gelled and liquid propellants are similar in terms of chemical stability during storage and thermal stability during the combustion process, investigations in the past concentrated on typical gelled fuels like MMH (Monomethylhydrazine) and UDMH (Unsymmetrical dimethylhydrazine), DMAZ (2-Dimethylaminoethylazide), and also different types of hydrocarbon fuels like JP-5, JP-8, JP-10 and RP-1. Typical oxidizers are WFNA (White fuming nitric acid), IRFNA (Inhibited red fuming nitric acid) and NTO (Nitrogen tetroxide)[9]. For the generation of a gel, two different groups of gelling agents exist: inorganic gellants, which stay unburned, and organic gellants. The most common inorganic gelling agent is silica, which is especially used to produce gelled nitric acid. Typical organic gelling agents are cellulose based derivatives like HPC (Hydroxypropylcellulose), HEC (Hydroxyethylcellulose) and HAC (Hydroxyalkylcellulose). Most promising combinations of gelled propellants for rocket applications are similar to liquid hypergol combinations, however also metallic additives like aluminium, magnesium or boron powder may be added to the propellants to increase the performance: MMH/Al/IRFNA and MMH/Al/NTO.

Advantages of gelled propellants in comparison with typical liquid and solid propellants are almost liquid-propellant like high performance, wide range thrust control and re-ignitability in addition to a solid-propellant like good storage behavior and safety aspects, as shown in Table 1. Storage stability is a very important factor for long-time applications and a further advantage of gelled propellants compared to some liquid propellants, for example hydrogen peroxide (H_2O_2) systems have to be vented continuously to prevent overpressure in the tank [6]. However, disadvantages of gelled fuels are the different atomization and burning process as well as higher pressure losses due to higher viscosities and therewith connected higher loads for the propellant feed system compared with typical liquid rocket engines. For that reason, gels envisaged for the application in a rocket

Table 1: Comparison of different propellants

requirement	liquid	solid	gel
easy to handle	-	+	+
performance	+	-	+
re-ignitable	+	-	+
throttleability	+	-	+
safety aspects	-	+	+
system complexity	-	+	+
storage stability	-	+	+

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[*] Post Doctoral Scientist, Purdue University, School of Aeronautics and Astronautics, Maurice J. Zucrow Laboratories, 500 Allison Road, West Lafayette, IN 47907, USA, AIAA Member, Email: arnold17@purdue.edu

[†] Ph.D. Student, Graduate Research Assistant, Purdue University, Department of Agricultural & Biological Engineering, 225 South University Street, West Lafayette, IN 47907, USA, Email: psantos@ecn.purdue.edu

[‡] Graduate Student, School of Aeronautics and Astronautics, Maurice J. Zucrow Laboratories, 500 Allison Road, West Lafayette, IN 47907, USA, Email: tkubal@purdue.edu

[§] Professor, Purdue University, Department of Agricultural & Biological Engineering, 225 South University Street, West Lafayette, IN 47907, USA, Email: campa@purdue.edu

[¶] Associate Professor, Purdue University, School of Aeronautics and Astronautics, 701 West Stadium Avenue, West Lafayette, IN 47907, USA, AIAA Senior Member, Email: wanderso@purdue.edu

propulsion system have to show a shear-thinning (viscosity of the gel decreases with an increasing shear rate) and thixotropic (viscosity of the gel decreases in time when a constant shear rate is applied) behavior [8].

2 Non-Newtonian fluids

On the contrary to a Newtonian fluid, for a non-Newtonian liquid the viscosity η is dependent on the applied shear rate $\dot{\gamma}$. For the characterization of Newtonian and non-Newtonian fluids without a yield point, the power-law model (Ostwald-de Waele model) is the most common correlation [4]:

$$\eta = K\dot{\gamma}^{n-1} \qquad (1)$$

K is the consistency index, whereas n gives the power-law index of the fluid. For $n = 1$ equation (1) describes a Newtonian fluid. However, shear thinning behavior is given for a power-law index $0 < n < 1$, and shear thickening (dilatant behavior) for $n > 1$ (see Figure 1 for different types of fluids).

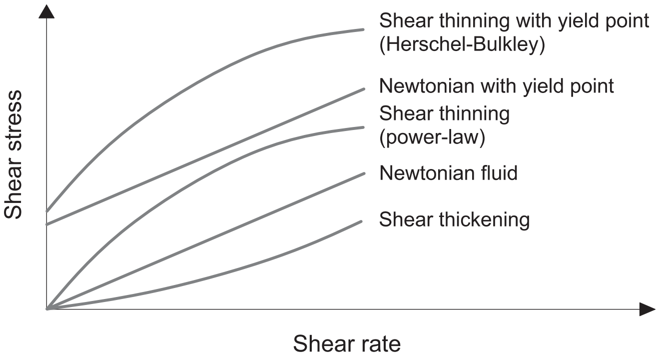


Figure 1: Newtonian and non-Newtonian fluids [8]

3 Propellant description

3.1 Fumed silica as a gelling agent

Untreated fumed silica SiO_2 (CAB-O-SIL® grade M-5) has been used to produce gelled hydrocarbon propellants for the present investigations to increase viscosity and thixotropy of the pure hydrocarbon fuels JP-8 and RP-1. In general, silica results from a combustion process of silicon tetrachloride ($SiCl_4$) in a H_2/O_2 flame (see equation (2)). Due to agglomeration a white, non-porous and fluffy powder is created with an agglomeration size of less than $44 \cdot 10^{-6}$m and a hydrogen chloride level of less than 60 ppm after a following calcining process. The aggregate chains of the silica are hereby a composition of fused together single particles [2].

$$SiCl_4 + 2H_2 + O_2 \xrightarrow{2070\ \text{K}} SiO_2 + 4HCl \qquad (2)$$

Table 2: Properties of CAB-O-SIL® M-5 [3]

B.E.T surface area (m^2/g)	200
tamped density (g/l)	50
specific gravity (g/cm^3)	2.2
average particle length (10^{-6}m)	0.2. . . 0.3
assay (% SiO_2)	> 99.8
melting point (K)	≈ 1983

Table 2 gives an overwiew of typical properties of CAB-O-SIL® M-5. The surface of the silica has hydrophilic characteristics and is capable of building up hydrogen bondings to create a gel when mixed with the pure liquid due to chemical groups – isolated hydroxyl groups (hydrophilic), hydrogen-bonded hydroxyl groups (hydrophilic) and siloxane groups – which are attached to the surface of the silica during the formation process. Due to the hydrogen bondings between single silica aggregates in a dispersed liquid system, increased viscosity and thixotropic behavior is the result. The application of a shear force destroys the hydrogen bondings between the aggregates and results in a reduced viscosity. However, when the shear stress is removed from the system, hydrogen bondings redevelop and increase the viscosity of the gel to its original value before the application of the shear stress, as depicted in Figure 2.

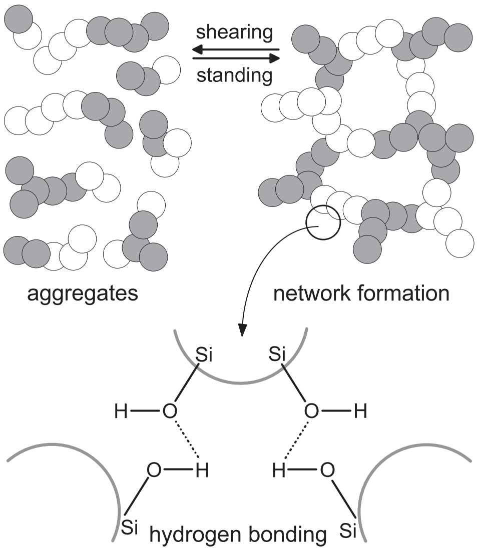


Figure 2: Silica aggregates, hydrogen bonding and network formation (according to [2])

The quality of the network between the aggregates is thereby a function of the following main parameters [2]:

- nature of the pure liquid
- concentration of gelling agent
- degree of dispersion
- temperature of the system

In combination with non-hydrogen-bonding liquids like aliphatic (no existence of aromatic rings, e. g. CH_4) and aromatic hydrocarbons and mineral oils, the single silica particels only can connect to each other, which results in a best possible network and also requires the lowest amount of silica (3…6 % by total weight) to obtain desired rheological behavior. On the other hand, in combination with highly hydrogen-bonding-systems like acids, alcoholes and ketones a much higher amount of silica is needed due to undesirable bondings between the silica surface and the liquid system. In terms of a high dispersion of the silica particles and the built-up of stable hydrogen bondings, a high shear rate during the mixing process and an adequate lenght of shearing time is fundamental, as the comparison of different mixing types showed impressively during the present investigations (see chapter 5.1).

3.2 Hydrocarbon fuels

Two different hydrocarbon fuels have been gelled with fumed silica for the present paper: Rocket propellant RP-1 and jet propellant JP-8. RP-1 (refined petroleum/rocket propellant) is a rocket propellant, which powers the first-stage boosters of the Delta and Atlas-Centaur rockets, and was also used in the first stage of the Saturn V moon rocket. Due to it's high density in comparison with the high-energetic liquid hydrogen (LH_2), the propellant combination RP-1/liquid oxygen (LOX) is also used in a great many of Russian booster engines (RD-170, RD-180) [10, 11]. JP-8 (jet propellant; NATO code F-34) is the U.S. Air Force primary jet fuel, replacing JP-4 in 1995 because of its less flammable character, better safety and higher combat survivability. Typical properties of the investigated hydrocarbon fuels JP-8 and RP-1 are summarized in Table 3.

Table 3: Fuel properties (at 293 K) [13, 12, 5, 7]

	JP-8	RP-1
gravity (g/cm^3)	0.755…0.84	0.81…0.85
viscosity (10^{-6}m^2/s)	$< 8^a$	1.96…2.24
flash point (K)	min. 310	316
boiling point (K)	430…573	420

^{a}at 253 K

4 Measuring system

For the detection of the rheological behavior of the gelled hydrocarbons a rotational rheometer operated in controlled rate mode (CRR) has been used. The rotational rheometer imposes strain to the liquid and measures the resulting stress for shear rates up to 1000 $^1/_s$. Most common test geometries for rotational rheometers are the parallel plate and the cone and plate (see Figure 3). Whereas the parallel plate offers some advantages like easy sample preparation, the cone and plate configuration has been used for the present investigations because it allows a homogeneous strain distribution in the gelled liquid. A temperature control system inside the equipment ensured a constant fluid temperature of 298 K during all rheological measurements.

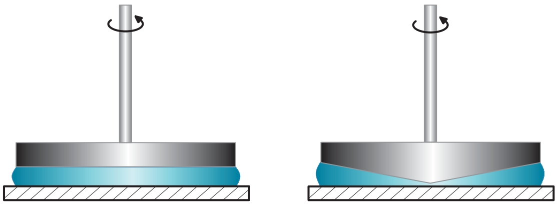


Figure 3: Basic geometries for a rotational rheometer: parallel plate (left), cone and plate (right)

5 Experimental results

The following sections describe the experimental results in terms of the gel mixing process, gel quality and stability, as well as rheological characterization of the gelled hydrocarbon fuels.

5.1 Mixing process and gel quality

A comparison between a conventional low-shear and an acoustic high-shear mixing technique (Resodyn ResonantAcoustic® LabRAM) has been carried out to determine the influence of the mixing process on the final gel quality. Due to the stiffness of the gel immediately after starting the mixing process, problems arise to keep the liquid in the mixing zone when using a conventional mixing blade or impeller. On the other hand, the acoustic mixing process uses low-frequency, high-intensity acoustic energy, resulting in a uniform shear level inside the mixing container. For the mixing, the entire system oscillates in resonance, which results in a very high dispersion in the mixing container. Micro-scale turbulences are created inside the medium by the acoustic waves, which gives a very consistant mixing result also for highly viscous or even solid materials in combination with a very short mixing time. Due to accelerations up to 100 g, very high shear rates are applied to the material [1].

Figure 4 shows the comparison of the high-shear acoustic and conventional mixing process for JP-8 fuel, using 4 %, 5 % and 6 % fumed silica (see also Table 4). Espe-

Table 4: Gel mixing process

	acoustic	conventional
gel composition	JP-8 / silica	JP-8 / silica
mixing time (s)	240	≈ 4000
rotating speed (1/s)	-	≈ 10
resonance frequency (Hz)	61.3	-

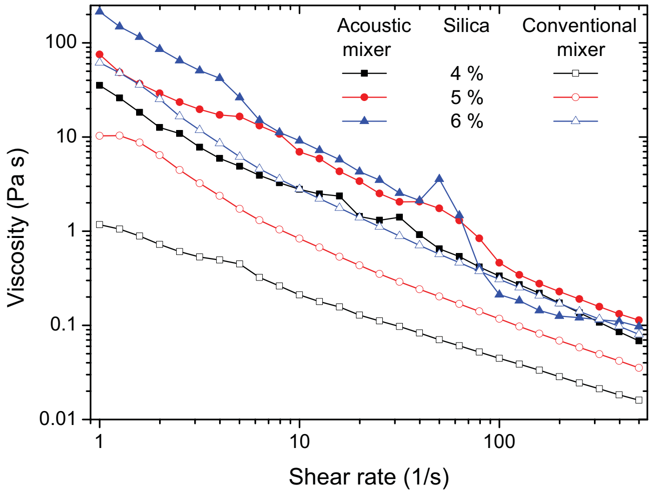


Figure 4: Comparison of high-shear acoustic and conventional mixing process for JP-8 and silica

cially for low shear rates $1 \ldots 10\ {}^{1}/_{s}$ the differences in measured viscosity between acoustic and conventional mixing are significant with a more than one order of magnitude higher viscosity for the investigated silica amounts of 4 %, 5 % and 6 % when using the high-shear acoustic mixing process. For a higher shear rate up to $1000\ {}^{1}/_{s}$, viscosity differences between the two mixing processes still exist, even though are less distinctive. Due to the convincing results, all following results have been generated by use of the acoustic mixing process.

Figure 5 depicts accelerations of approx. 50 g and 100 g and appropriate resonance frequencies for typical propellant mixing processes with varying mixing times for JP-8 and 5 % silica using the acoustic technique. Acceleration and resonance frequency attain constant values after a very short mixing time of approx. $10 \ldots 15$ s, however with an acceleration of 50 g a slightly lower freqency was found in comparison to the 100 g mixing processes.

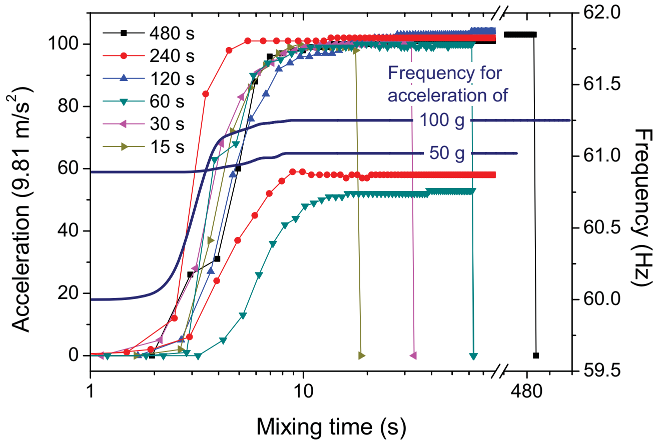
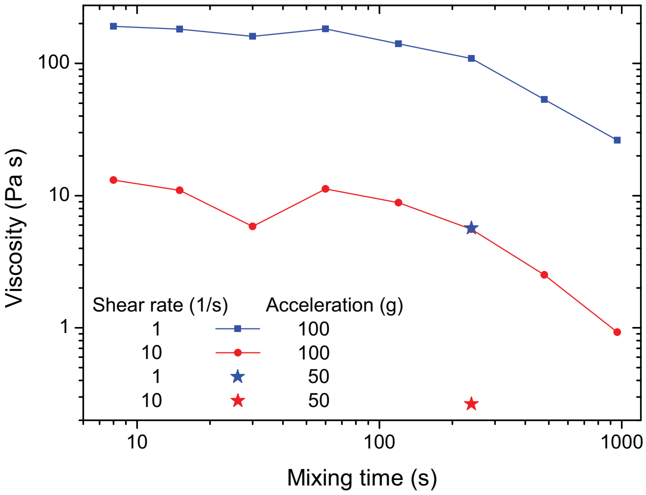


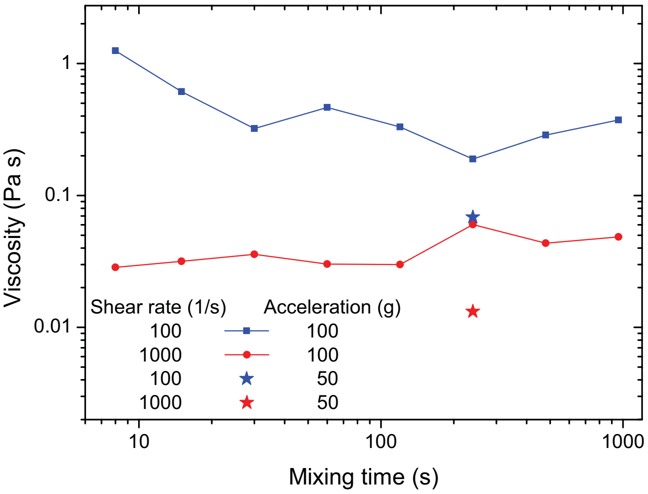
Figure 5: Gel mixing process with acoustic mixing technique (JP-8 with 5% silica)

5.2 Mixing time vs. gel quality

Based on the results of section 5.1, a concentration of 5 % silica together with JP-8 fuel has been choosen to investigate the influence of the mixing time on the quality of the mixed gel, as shown in Figure 6 for mixing times in the range of 8 s up to 960 s. As can be seen, a higher mixing time does not come along with a higher viscosity of the mixed gel. In contrast however, a shorter mixing time seems to improve the quality of the gel in terms of viscosity, not only for low shear rates in the range of $1 \ldots 10\ {}^{1}/_{s}$ (see Figure 6 (a)), but also fewer distinctively for higher shear rates up to $1000\ {}^{1}/_{s}$ (see Figure 6 (b)). Especially for low shear rates, a significant decrease in viscosity can be seen for mixing times exceeding 80 s. Due to very high accelerations during the mixing process (see Figure 5) the loss in viscosity for higher mixing times can be caused by interactions of the liquid with the hy-



(a) Low shear rate



(b) High shear rate

Figure 6: Gel viscosity as a function of mixing time and mixing acceleration (JP-8 with 5% silica)

drogen bondings of the silica particles [2], which affects and weakens the hydrogen bondings between the silica particles (see Figure 2). In comparison however, with a reduced mixing acceleration of only 50 g instead of 100 g, it seems not to be possible to produce a gel with similar high viscosities even for a much longer mixing time (see Figures 6 (a) and 6 (b)). Based on these results, a mixing time of 60 s and mixing accelerations of approximately 100 g have been choosen to assure a preferably and reproducible gel quality.

In order to characterize the stability of the gel, centrifuge tests have been conducted with JP-8 and a silica amount of 5 %, applying two constant accelerations of approx. 1500 g (3600 rpm) and approx. 90 g (900 rpm) for a time of 600 s in each case (see Figure 7). It is a remarkable result to state that the rheological properties of the gel change significantly for different mixing times as shown in Figure 6, however this behavior is not related to the phase separation in terms of gel stability (see Figure 7). The influence of the mixing time on the stability of the gel seems to be almost negligible with only a slight decrease of the remaining gel mass for a higher mixing time.

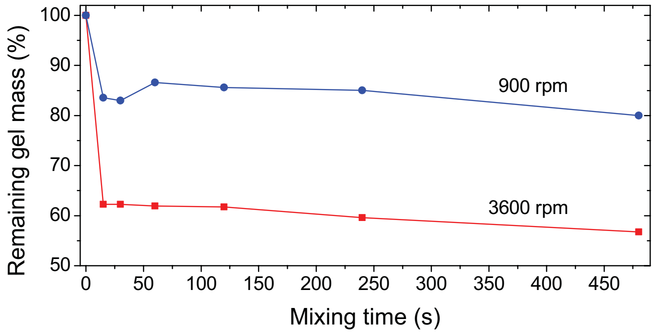


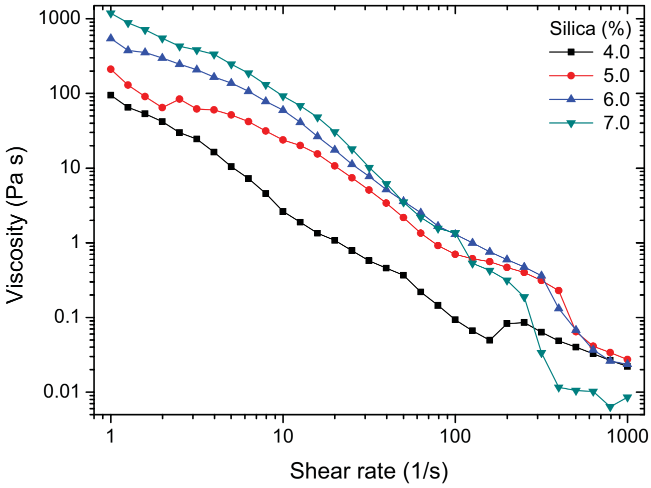
Figure 7: Gel stability as a function of mixing time (JP-8 with 5% silica)

5.3 Rheological characterization

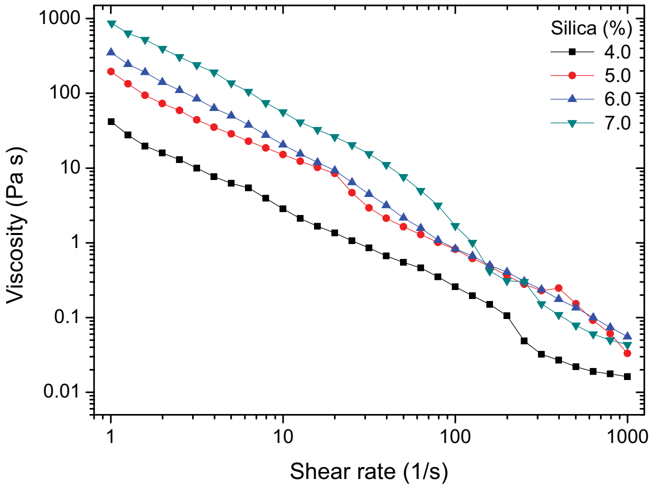
After describing the gel mixing process in section 5.1 and the determination of the optimum minimum mixing time and acceleration to obtain a best possible mixed gel in terms of a high viscosity in section 5.2, the following section will delve into the rheological behaviour of the gelled hydrocarbons like viscosity η vs. shear rate $\dot{\gamma}$ and gel stability as a function of silica amount in the range of 4 % up to 7 %.

5.3.1 Gel viscosity

Figure 8 depicts the comparison of the gel viscosity of RP-1 (Figure 8 (a)) and JP-8 (Figure 8 (b)) for shear rates in the range from $1\,{}^{1}/_{\mathrm{s}}$ to $1000\,{}^{1}/_{\mathrm{s}}$ as a function of the added silica amount. A significant increase of the viscosity for both hydrocarbon fuels can be stated with an increasing gelling agent mass. The influence of the fumed silica is not only visible for low shear rates but remains noticeable with a lower significance up to high shear rates. However, for shear rates up to approximately $100\,{}^{1}/_{\mathrm{s}}$ a slightly higher viscosity behavior of the RP-1 gel in comparison to the JP-8 gel has been measured.



(a) Rocket propellant RP-1



(b) Jet propellant JP-8

Figure 8: Gel viscosity as a function of silica amount

5.3.2 Gel stability

To simulate the acceleration and vibration loads during a typical rocket launch, which can cause gel separation in the tank and propellant feed system, centrifuge tests have been conducted. The gel stability as a function of the silica amount is illustrated in Figure 9 for a centrifuge operating time of 600 s. After the centrifuge tests, the separated liquid due to the acceleration has been compared with the initial propellant mass to describe the stability of the investigated gels. Figure 9 indicates, that

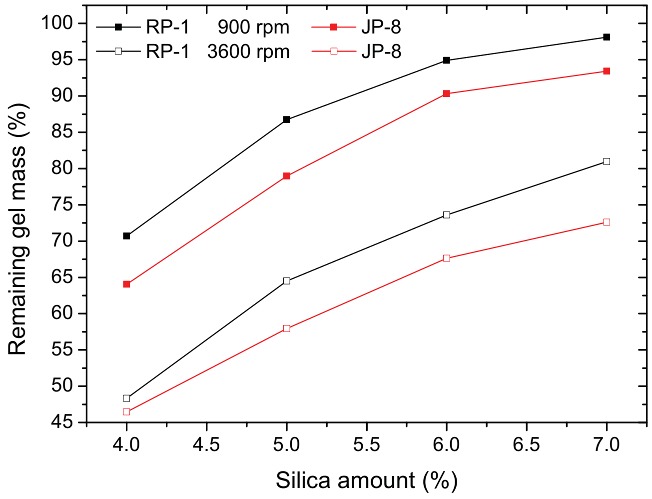


Figure 9: Gel stability as a function of silica amount

the 6 % and 7 % gels are quite stable for accelerations of approx. 90 g (900 rpm), whereas for accelerations of approx. 1500 g (3600 rpm) only 70 . . . 80 % of the initial gel mass is remaining. Silica amounts of less than 6 % did not show a stable behaviour during this investigations even for the 90 g accelerations. However, the RP-1 gel seems to be more stable than the JP-8 gel within in the investigated range of added gelling agent and applied accelerations. These results are consistent with the investigated gel viscosity in section 5.3.1, where the measurements have shown a slightly higher viscosity for the RP-1 gel in comparison to the JP-8 gel.

6 Conclusions and future work

Within the present study, two gelled hydrocarbon fuels, JP-8 and RP-1, have been investigated experimentally, using fumed silica as a gelling agent and acoustic mixing technology to produce the gels. The influence of the mixing time turned out to be a major parameter for the gel quality, whereas a relatively short mixing time resulted in gels with the highest viscosity. The amount of the added gelling agent showed significant influence on the viscosity of the gels for low as well as high shear rates. Future investigations at Purdue University not only will implicate gelled hydrocarbon fuels like JP-8, JP-10 and RP-1, but also consider the rheological behavior of rocket engine fuel MMH (monomethylhydrazine, $CH_3N_2H_3$), using organic cellulose-based gelling agents like hydroxypropylcellulose (HPC) and hydroxyethylcellulose (HEC).

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